

## The Crystal Structure of Boleite—A Mineral Containing Silver Atom Clusters

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Received March 10, 1972

The mineral boleite,  $\text{Pb}_{26}\text{Ag}_9\text{Cu}_{24}\text{Cl}_{62}(\text{OH})_{48}$ , is cubic, space group  $Pm\bar{3}m$ , with  $a = 15.29 \text{ \AA}$ . Lead and silver atoms form a distorted body-centered array leading to octahedral groupings of these atoms. The silver atoms and their coordinating chlorines form  $\text{Ag}_6\text{Cl}_8\text{Cl}_6$  groups similar to those in the metal cluster compounds  $\text{MoCl}_2$  and  $\text{WCl}_2$ . Lead and copper atoms are in distorted square antiprismatic and tetragonal bipyramidal coordination, respectively.

### Introduction

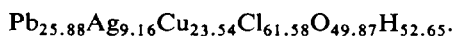
Boleite is a lead copper oxychloride mineral which occurs as deep blue crystals of cubic form. These cubes are zoned and consist of an optically isotropic or quasi-isotropic core and a birefringent outer rim of complex structure. The cube faces are sometimes occupied by epitaxial overgrowths of the related species pseudoboleite and cumengite. Boleite has been studied in detail by Mallard and Cumenge (1), Friedel (2), and Hocart (3). They all considered the birefringent material to be tetragonal and untwinned and the isotropic core to be pseudocubic due to twinning. Hadding (4) and Gossner (5), however, concluded that boleite was truly cubic. Ito (6) proposed a tetragonal structure based upon twinning of cubic units at the unit cell level. The tetragonal twinned cell has a "twinned space group"  $I4/mmm$  and parameters  $a = 15.27$  and  $c = 60.94 \text{ \AA}$ . It consists of four cubic cells stacked along [001] and related by mirror planes at  $z = \frac{1}{4}$  and  $\frac{3}{4}$  and by a glide plane at  $z = \frac{1}{2}$ .

In a restudy of the boleite group Winchell (7) concluded that the outer rim of boleite is either an intergrowth of two species (perhaps boleite and pseudoboleite) or consists of boleite lamellae having different orientations. He also performed heating stage experiments on boleite between 25 and 265°C where crystal decomposition began. Between 80 and 180°C the color changed

gradually from blue to green, while the birefringent rim and the quasi-isotropic core merged into an apparently homogeneous, isotropic phase. Upon cooling, the blue color returned but the isotropy persisted. From these and other observations Winchell proposed that boleite undergoes an inversion from a pseudocubic form to a cubic one with increasing temperature.

### Symmetry and Composition

To determine the true symmetry of boleite, isotropic cleavage fragments were examined by the author using the Weissenberg and precession methods and  $\text{CuK}\alpha$  and  $\text{MoK}\alpha$  radiation. As reported by (4) and (5), isotropic boleite is cubic, space group  $Pm\bar{3}m$ , with no evidence of twinning. The unit cell parameter, as determined from Bradley-Jay extrapolations of single-crystal diffractometer data, is  $a = 15.29 \text{ \AA}$ . Unit cell contents calculated from the chemical analysis of isotropic boleite reported in (2) are



A qualitative chemical analysis with the electron microprobe showed Pb, Ag, Cu, and Cl as the only elements present. Oxygen was not determined due to instrumental limitations. The above results accord well with the formula  $\text{Pb}_{26}\text{Ag}_9\text{Cu}_{24}\text{Cl}_{62}(\text{OH})_{48}$  determined by crystal structure analysis. The observed and calculated densities are 5.054 and 5.062 g/cm<sup>3</sup>, respectively.

\* Contribution No. 306, The Mineralogical Laboratory.



TABLE I—continued

<i>h</i>	<i>F</i> <sub>obsd</sub>	<i>F</i> <sub>calcd</sub>	<i>h</i>	<i>F</i> <sub>obsd</sub>	<i>F</i> <sub>calcd</sub>	<i>h</i>	<i>F</i> <sub>obsd</sub>	<i>F</i> <sub>calcd</sub>	<i>h</i>	<i>F</i> <sub>obsd</sub>	<i>F</i> <sub>calcd</sub>	<i>h</i>	<i>F</i> <sub>obsd</sub>	<i>F</i> <sub>calcd</sub>
(9, 2)			(5, 3)—(continued)			(4, 4)—(continued)			(9, 4)			(6, 6)—(continued)		
9	114	137	12	266	238	8	1167	1028	9	432	438	10	364	363
			13	225	158	9	569	565	10	543	529	11	491	550
(3, 3)			(6, 3)			10	1203	1284	(5, 5)			(7, 6)		
3	1312	1343	6	673	610	11	149	200	5	507	400	7	856	723
4	188	150	7	480	434	12	312	376	6	394	341	8	276	263
5	1447	1424	8	121	28	(5, 4)			7	954	859	9	120	35
6	415	387	9	125	179	5	460	421	8	846	816	10	371	351
7	836	784	10	394	439	6	211	146	9	1171	1117	11	263	276
8	295	285	11	197	177	7	373	330	10	96	142			
9	311	270	12	84	152	8	441	366	11	510	481	(8, 6)		
10	404	400	13	188	205	9	563	506	12	332	370	8	257	254
11	1310	1456	(7, 3)			10	394	365	(6, 5)			9	120	9
12	327	350	7	954	861	11	211	271	6	117	102	10	354	354
13	169	106	8	331	332	12	152	147	7	120	101			
(4, 3)			9	438	427	13	401	404	8	478	442	(7, 7)		
4	647	581	10	455	452	(6, 4)			9	126	182	7	1038	931
5	721	670	11	1026	1075	6	388	300	10	309	320	8	124	102
6	348	318	12	124	97	7	448	406	11	410	485	9	320	353
7	115	7	(8, 3)			8	368	313	12	470	472	10	599	582
8	483	441	8	108	95	9	230	186	(8, 5)			11	1034	1090
9	383	360	9	163	60	10	102	60	8	919	863	(8, 7)		
10	91	22	10	440	507	11	91	64	9	471	442	8	418	406
11	197	199	11	227	335	(7, 4)			10	406	426	10	105	116
12	88	94	12	307	372	7	309	274	11	301	305			
13	74	133	(9, 3)			8	342	288	(9, 5)			(9, 7)		
(5, 3)			9	113	228	9	176	97	9	614	684	9	285	344
5	1011	926	10	175	221	10	200	148	10	122	201	(8, 8)		
6	108	62	11	227	250	11	88	5	11	190	200	8	474	482
7	825	690	(4, 4)			(8, 4)			(6, 6)			9	355	341
8	416	393	4	671	560	8	439	409	6	885	811	10	846	853
9	668	667	5	931	814	9	257	251	7	606	591			
10	655	726	6	824	698	10	364	363	8	120	46	(9, 8)		
11	266	240	7	521	473	11	243	206	9	283	236	9	336	335

<sup>a</sup> The indices for (*k*, *l*) are given in parentheses above each grouping.

### Structure Determination

Using an isotropic cleavage fragment of dimensions  $0.08 \times 0.14 \times 0.40$  mm and equi-inclination Weissenberg geometry, a total of 1560 intensities were measured on an automated single-crystal diffractometer. Graphite flat-crystal mono-chromated  $\text{CuK}\alpha$  radiation and pulse height analysis were employed. The data were corrected for Lorentz, polarization, and absorption effects. Symmetrically equivalent reflections were then averaged to obtain the final set of 360  $|F|_{\text{obsd}}$  values.

The data were then used to calculate the Patterson function of boleite. Interatomic vectors were also calculated from the atomic positions in Ito's untwinned cubic structure. Comparison of the two vector sets showed that two of the five cation sites in Ito's structure were occupied by heavy atoms. Starting with these two atoms, the rest were located by means of successive electron density syntheses.

Refinement of the structure was carried out by the method of least-squares using the IBM 360 program SFLSQ5 written by C. T. Prewitt.

TABLE II

POSITIONAL AND THERMAL PARAMETERS IN BOLEITE<sup>a</sup>

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
Pb(1)	0.2269(5)	½	½	1.4(2)
Pb(2)	0.3030(2)	0.3030	0.3030	1.0(1)
Pb(3)	0.2734(3)	½	0	1.4(1)
Ag(1)	0	0.1561(10)	0	2.2(3)
Ag(2)	0	½	0	3.2(5)
Cu	0.2563(5)	0.2563	0.0925(7)	0.7(2)
Cl(1)	0.1233(16)	0.1233	0.1233	2.4(8)
Cl(2)	0.3864(10)	0.3864	0.1218(15)	2.0(4)
Cl(3)	0	0.3354(32)	0	2.0(9)
Cl(4)	0.1311(14)	½	0.1311	1.9(7)
Cl(5)	0.3282(14)	½	0.3282	1.9(6)
OH(1)	0	0.3218(30)	0.2060(30)	0.2(10)
OH(2)	0.1831(28)	0.1831	0.3300(43)	3.3(14)

<sup>a</sup> Standard errors to the least significant digit are shown in parentheses.

Scattering factors for Pb<sup>+</sup> and Ag<sup>+1/2</sup> were obtained from Cromer and Waber (8), Cu<sup>+</sup> and Cl<sup>-1/2</sup> from Doyle and Turner (9), and O<sup>-</sup> from the "International Tables for X-ray Crystallography" (10). Anomalous dispersion corrections for Pb, Ag, Cu, and Cl were taken from Cromer (11). Refinement was carried out using isotropic atomic temperature factors. All reflections, excluding  $F_{\text{obsd}} < F_{\text{min}}$ , were equally weighted. The final *R* value is 10.5% for all reflections or 8.9% if the unobserved reflections are excluded. Table I contains a list of structure factors and Table II, the refined atomic parameters. Interatomic distances and their standard errors (Table III) were calculated with the program ORFFE of Busing, Martin, and Levy (12) using the variance-covariance matrix for atomic coordinates.

### Structure and Bonding

Although the unit cell of boleite corresponds to that found by Ito, his proposed crystal structure is quite different from the one described here. Before giving a detailed description of this complex structure, it is desirable to provide a brief overview.

The structure of boleite is based upon a distorted body-centered framework of lead and silver atoms. Only the three Ag(2) atoms are not part of the body-centered array. Since an octahedron may be inscribed within a pair of body-

TABLE III

INTERATOMIC DISTANCES<sup>a</sup> (IN Å)

Pb(1)–4 Cl(2)	2.94(2)	Cl(1)–3 OH(2)	3.41(8)
4 Cl(5)	3.05(1)	3 Cl(1)	3.77(5)
Pb(2)–3 OH(2)	2.63(6)	6 OH(1)	3.79(4)
3 Cl(5)	3.06(1)	Cl(2)–2 OH(2)	3.36(4)
3 Cl(2)	3.31(2)	2 OH(1)	3.47(4)
Pb(3)–2 OH(1)	2.91(5)	2 Cl(2)	3.47(3)
2 Cl(4)	2.96(1)	2 Cl(5)	3.71(2)
4 Cl(2)	3.08(1)	Cl(2)	3.72(5)
2 Pb(3)	4.900(7)	Cl(3)–4 OH(1)	3.16(5)
2 Pb(1)	4.903(6)	4 Cl(4)	3.79(4)
Ag(1)–4 Cl(1)	2.71(3)	4 OH(2)	3.96(6)
Cl(3)	2.74(5)	Cl(4)–2 OH(2)	2.83(6)
4 Ag(1)	3.38(2)	4 OH(1)	3.57(4)
Ag(2)–2 Cl(3)	2.52(5)	2 Cl(4)	4.01(4)
4 Cl(4)	2.83(3)	Cl(5)–4 Cl(5)	3.71(3)
Cu–2 OH(1)	1.90(3)	OH(1)– OH(1)	2.50(9)
2 OH(2)	2.11(4)	2 OH(2)	2.82(4)
Cl(2)	2.85(2)	OH(2)–2 OH(2)	3.18(11)
Cl(1)	2.91(3)		
Cu	2.83(2)		
Pb(2)	3.37(1)		
2 Cu	3.54(2)		

<sup>a</sup> Standard errors in parentheses.

centered cubic cells, this arrangement leads to octahedral groupings of lead and silver atoms in boleite. Coordinated to the faces and vertices of the metal polyhedra are chlorine atoms. These chlorines are shared with Ag<sub>2</sub>(Cl)<sub>6</sub> and Cu(OH)<sub>4</sub>Cl<sub>2</sub> distorted octahedra such that the anion polyhedra form bridges between the metal polyhedra. Individual lead atoms are coordinated by distorted square antiprisms of chlorine and hydroxyl ions. These antiprisms are linked in a complex fashion by shared faces and vertices. The octahedra around the copper atoms are likewise linked by shared edges.

Looking at the structure in detail, the Ag(1) atoms form a regular octahedron centered at the unit-cell origin. Eight Cl(1) atoms are located above the faces of the octahedron and six Cl(3) atoms lie adjacent to the six octahedral vertices (Fig. 1). This is the same configuration found in the well-known metal cluster compounds NbI<sub>1.83</sub>, MoCl<sub>2</sub>, WCl<sub>2</sub>, and their derivatives (13). By analogy, boleite is a metal cluster compound, the first reported involving silver and a halogen. Silver(I) dipropylthiocarbamate contains a distorted Ag<sub>6</sub> octahedron (14), but the silver-anion arrangement is unrelated to that in boleite.

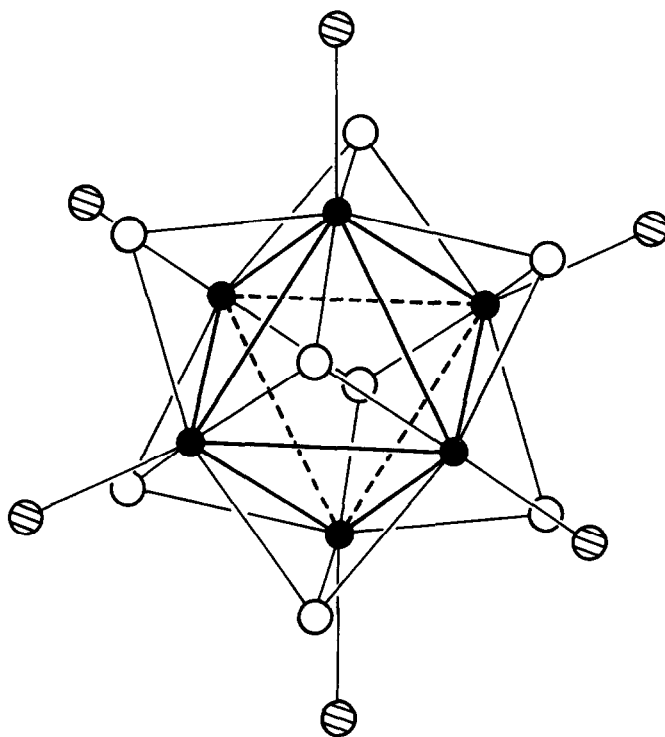


FIG. 1. The  $\text{Ag}_6\text{Cl}_8\text{Cl}_6$  group in boleite.

Within the  $\text{Ag}_6$  octahedron of boleite the Ag–Ag distance is 3.38 Å. This is longer than in silver metal (2.89 Å) and no claim is made here for the existence of metal–metal bonds in boleite. The Ag(1) octahedron, which is centered at 000, shares Cl(3) atoms with three Ag(2)Cl<sub>6</sub> tetragonal bipyramids. The latter are centered at  $\frac{1}{2}00$  and equivalent positions. Along the unit cell edges the sequence of polyhedra is therefore  $\text{Ag}_6$  octahedron—AgCl<sub>6</sub> bipyramid— $\text{Ag}_6$  octahedron. Ag(1) is coordinated by four chlorine atoms at 2.71 Å and one more at 2.74 Å. These Ag–Cl distances are comparable to that in AgCl (2.77 Å) and to the sum of the covalent radii, 2.78 Å (15). Ag(2) is coordinated by two chlorine atoms at 2.52 Å and another four at 2.83 Å. Analogously, in  $\text{Cs}_2\text{AgAuCl}_6$  (16), there are distorted AgCl<sub>6</sub> octahedra which have two Ag–Cl distances of 2.36 Å and four more of 2.92 Å. The two short bonds result from the tendency of Ag<sup>I</sup> to form pairs of linear covalent bonds.

Also of interest are the nearly regular Pb<sub>6</sub> octahedra centered at  $\frac{1}{2}\frac{1}{2}0$  and equivalent positions. Here the Pb–Pb distances are 4.900 and 4.903 Å, which are much greater than in lead metal (3.50 Å). Above each octahedron face is a Cl(2) atom, but there are no anions adjacent

to the vertex metal atoms as in the silver octahedron.

Pb(1), Pb(2), and Pb(3) are coordinated by distorted square antiprisms of chlorine and/or hydroxyl ions such as in diableite,  $\text{Pb}_2\text{Cu}(\text{OH})_4\text{Cl}_2$  (17). The antiprism around Pb(2) is grossly distorted and includes a ninth ligand. Pb–OH distances in these polyhedra are 2.63 and 2.91 Å, and Pb–Cl distances range from 2.94 to 3.31 Å. These are typical of distances in ionic lead oxychlorides (17). The Pb(1) and Pb(2) antiprisms share faces to form an eight-membered ring, and the Pb(3) antiprisms share edges to form a separate four-membered ring. Both rings are centered around the axis  $\frac{1}{2}\frac{1}{2}z$  and are joined by shared vertices.

Copper atoms are coordinated by two OH groups at 1.90 Å, another two at 2.11 Å, and two chlorine atoms at 2.85 and 2.91 Å. Together they form a distorted tetragonal bipyramid around the Cu<sup>+2</sup> ion. Each  $\text{Cu}(\text{OH})_4\text{Cl}_2$  bipyramid shares edges and a common vertex (A in Fig. 2) with two others to form a trimer around the [111] axis. Next, each trimer shares edges (BC and DE) with two other trimers. These two then share edges with a fourth to form a four-membered ring of trimers around the axis

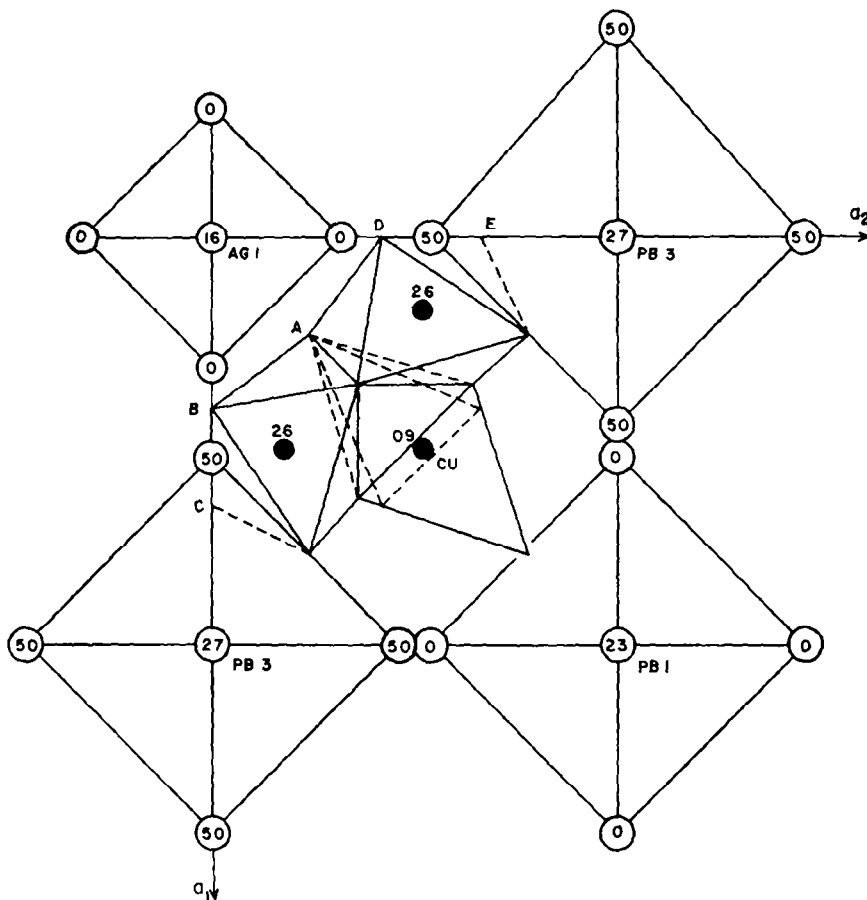


FIG. 2. Projection on (001) of  $\frac{1}{2}$  of the unit cell. Some atoms are omitted for clarity. The  $Ag_6$  and  $Pb_6$  octahedra are shown along with a trimer of Cu coordination polyhedra. Numerals are heights of atoms in  $z \times 100$ .

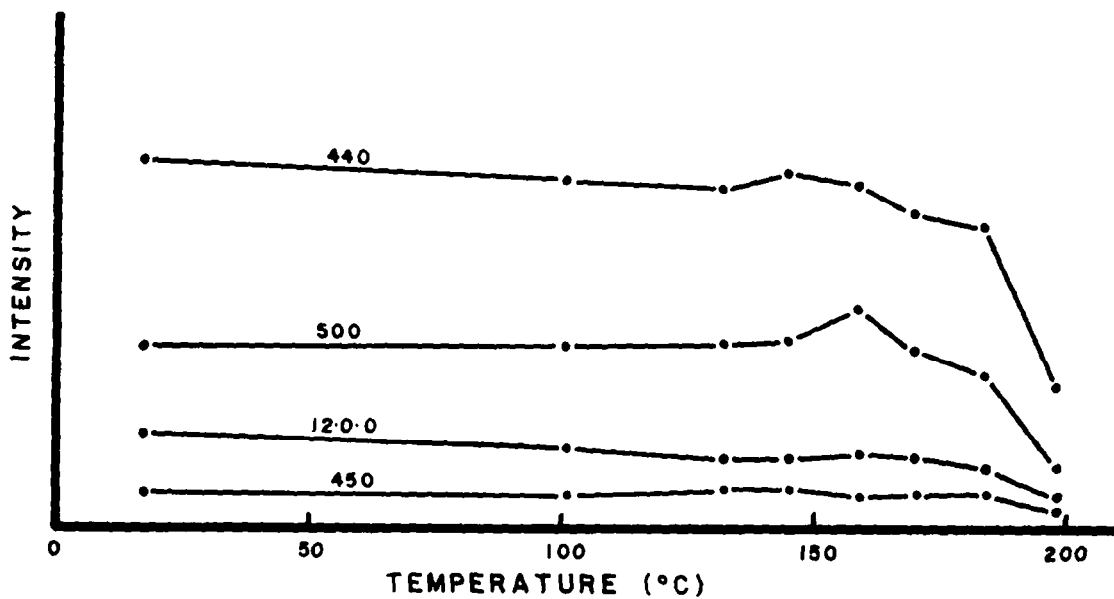


FIG. 3. Plot of integrated intensity vs temperature for several reflections.

00z. Since the basal plane of the unit cell is a mirror plane, the ring is duplicated by reflection in the next unit-cell down. Thus, there are two rings, each composed of four trimers. These two rings are also joined by shared edges. Cu-Cu distances across these shared edges are very short (2.83 Å) compared to those within an individual trimer (3.54 Å). The very short OH(1)-OH(1) separation of 2.50 Å is the edge shared between trimers. To the author's knowledge, this configuration of copper coordination polyhedra is unique.

### High Temperature Study

In order to check the conclusions of (7) with respect to polymorphism in boleite, a cleavage fragment was mounted in a high temperature furnace attached to a single-crystal diffractometer. The intensities of four reflections were monitored (Fig. 3) as the crystal was slowly heated from 17 to 251°C. The average heating rate was about 9°C/hr. No significant change occurred until ~160°C when the intensities of all reflections began to decrease noticeably. When the crystal was examined by eye at 198°C, its color had changed from blue to black. After heating to 251°C and cooling, an X-ray powder photograph of the crystal was obtained. It showed only lines due to PbCl<sub>2</sub>, AgCl, and CuO. In summary, no evidence was found for an inversion in boleite. The intensity change above 160°C is due to crystal decomposition, the black coating being CuO. It should be noted that the heating rate in (7) was between 1° and 4°C/min, hence equilibrium was probably not attained. The blue to green color change may have been due simply to small changes in bond lengths within the copper coordination polyhedron producing changes in the crystal field splittings. The

attainment of complete isotropy probably resulted from the relief of strain in a cubic crystal.

### Acknowledgments

The author wishes to thank Dr. Donald R. Peacor and Dr. Billy J. Evans for reading the manuscript and making helpful criticisms.

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