achse parallel zu *a* enthalten. Durch die zweizählige Schraubenachse, welche die Symmetrie der Kette bedingt, lassen sich diese Ketten als Schrauben auffassen.

Im $BaGeO_3(h)$ liegen demnach Zweierketten mit Schraubencharakter vor, wobei, wie Fig. 5 zeigt, auf jede Elementarzelle ein Teil von zwei Zweierketten entfällt, die sich in ihrem entgegengesetzten Windungssinn unterscheiden.

Praktisch der gleiche Bau der Zweierketten wurde von Corbridge (1956) im Rubidiumphosphat $(RbPO_3)_n$ gefunden. Auch hier winden sich die Zweierketten um zweizählige Schraubenachsen und der pro Elementarzelle entfallende Teil von zwei verschiedenen Zweierketten setzt sich in entgegengesetzter Weise fort.

Herrn Prof. Dr. Dr. h. c. E. Thilo danke ich für sein ständiges Interesse an dieser Arbeit, Herrn Dr. G. Krüger für die Herstellung der Substanz, Fräulein J. Bethge und Herrn R. P. Holzapfel für die gewissenhafte Durchführung des grössten Teils der Rechenarbeit.

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The Crystal Structure of Salesite, $CuIO_3(OH)$*

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Salesite, $CuIO_3(OH)$ is orthorhombic, space group *Pnma*, with

$$a_0 = 10\cdot80,\ b_0 = 6\cdot71,\ c_0 = 4\cdot79\ \text{Å}\ .$$

Copper has a square planar co-ordination (Cu–OH 1·95 Å (×2) and Cu–O_2 2·01 Å (×2)), with two further oxygens (Cu–O_1 2·59 Å (×2)) completing a distorted octahedron. The iodine-oxygen distances within the trigonal-pyramidal iodate group are 1·78 Å and 1·82 Å (×2). The average O–I–O angle is 96·7°. Each iodine atom has three oxygen neighbors, in addition to the three in the iodate group. The structure of salesite is composed of copper octahedral chains, formed by sharing the bipyramidal edge, which are joined together by trigonal pyramidal iodate groups in a three-dimensional network.

Introduction

The exact configuration of the iodate group has been studied in very few compounds. Apart from the earlier studies on HIO_3 (Rogers & Helmholz, 1941), $NaIO_3$ (MacGillavry & van Eck, 1943; Náray Szabó & Neugebauer, 1947), $LiIO_3$ (Zachariasen & Barta, 1931), only recently the structures of $Ce(IO_3)_4.H_2O$ (Ibers, 1956), $Ce(IO_3)_4$ (Cromer & Larson, 1956), and $Zr(IO_3)_4$ (Larson & Cromer, 1961) have been determined with some precision. Salesite, $CuIO_3(OH)$ is a naturally occurring basic copper iodate, found from Chuquicamata, Chile (Palache & Jarrell, 1939). Its structure establishes the exact configuration of the iodate group and the stereochemistry of the cupric ion. A grain of this rare mineral (U.S.N.M. 105071) was obtained through the courtesy of Dr George Switzer of the U.S. National Museum, Washington, D.C. for the structure determination.

The crystal data

Salesite is orthorhombic, crystal class *mmm* (Palache & Jarrell, 1939). The unit-cell dimensions, determined from Weissenberg photographs taken with Cu $K\alpha$ radiation, are:

$$a_0 = 10\cdot80,\ b_0 = 6\cdot71,\ c_0 = 4\cdot79\ \text{Å}\ ,$$

giving axial ratios 1·6095:1:0·7139 compared with morphological values 1·6023:1:0·7439. The cell dimensions are in good agreement with those found by Richmond (in Palache & Jarrell, 1939). There are four formula units in the cell with $D_{\text{meas.}}$ 4·77 g.cm.$^{-3}$ and D_c 4·887 g.cm.$^{-3}$. From the systematic absences

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* Mitt. Nr. 133, Abteilung für Kristallographie und Strukturlehre.

($0kl$ for $k+l$ odd, $hk0$ for h odd) the space group is *Pnma* or $Pn2_1a$. The centrosymmetric space group *Pnma* was chosen for the structure determination in accordance with the crystal class evidence and was found subsequently to be correct.

The optical properties of salesite, as determined by Palache & Jarrell (1939), are given below:

Orientation		n	Pleochroism	
X	c	1·786	Colorless	Biaxial (negative)
Y	b	2·070	Light bluish green	$2V$ 0° to 5°
Z	a	2·075	Bluish green	$r > v$ extreme

There is a perfect cleavage parallel to (101).

An artificial orthorhombic $CuIO_3(OH)$ has been known for a long time (Granger & de Schulten, 1904). Since the refractive indices of this compound are consistently lower than those of salesite, it was considered to be a possible dimorph of salesite (*Dana's System of Mineralogy*, 1951). However, rotation and Weissenberg photographs of the artificial $CuIO_3(OH)$, prepared by Dr H. R. Oswald, indicate that it is identical with salesite in cell dimensions and the distribution of intensities.

Experimental

The $hk0$ and $h0l$ intensity data were collected by visual estimation from multiple-film Weissenberg photographs, taken with Mo $K\alpha$ radiation. The intensities were corrected for Lorentz and polarisation factors, but no absorption corrections have been made, since the crystal used was a very small cleavage fragment. All the calculations have been carried out on the Bull Gamma AET computer with programs, written by Dr Y. Iitaka (1961).

The determination of the structure

The refractive indices and the pleochroic colors, parallel to a and b, are similar, but are quite different from those parallel to c. These optical properties suggested that the copper–oxygen square co-ordination plane, as well as the iodate groups, are approximately parallel to ab.

There are 4 Cu, 4 (OH), 4 I and 12 O atoms in the unit cell. 4 Cu were placed in $4(a)$ 0, 0, 0 etc., 4 (OH) in $4(b)$ $0, 0, \frac{1}{2}$ etc., and 4 I in $4(c)$ $x, \frac{1}{4}, z$ etc. with $x \sim \frac{1}{4}$, $z \sim 0$ (or $\frac{1}{2}$). The (001) projection was first solved, from the known trigonal pyramidal configuration of the iodate group and the presence of the symmetry plane at $b=\frac{1}{4}$. 4 O were placed in $4(c)$ with $x=0{\cdot}38$, z and 8 O in $8(d)$ x, y, z etc., with $x=0{\cdot}19$, $y=0{\cdot}08$, z. A subsequent examination of the Weissenberg photographs showed that $hk0$ and $h0l$ reflections with $h+k=4n$ and $h+l=2n$ are very strong and hence confirmed the iodine position. The (001) projection was refined with this trial model till the R-factor was 0·17. A difference Fourier synthesis was calculated at this stage, which showed that the (OH) ion is located also in $4(c)$, with $x=0{\cdot}03$. In the following structure-factor calculation, including the (OH) ion in its correct position, the R-factor decreased to 0·14.

Structure factors calculated for the $h0l$ reflections, including the contribution of the copper atom at the origin and the iodine atom at $x=0{\cdot}244$ and $z=0$, yielded an R-factor of 0·22. A difference Fourier synthesis, calculated with only those $h0l$ reflections for which $h+l=2n$, whose signs have been unequivocally determined, indicated the locations of the oxygen atoms, along with some false peaks. The correct oxygen positions were chosen from the known configuration of the iodate group and the copper octahedron. These parameters were subsequently refined by the least-squares method. In the least-squares refinement program used, the function

$$\Sigma w(hkl)\{|F_o(hkl)|^2 - |F_c(hkl)|^2\}^2$$

was minimized. The standard deviation was calculated by

$$\sigma(x_j) = [\Sigma w(F_o^2 - F_c^2)^2/(m-s)]^{\frac{1}{2}} \cdot [1/\Sigma w(\partial F_c^2/\partial x_j)^2]^{\frac{1}{2}} ,$$

where m is the number of observations and s is the number of unknowns. A three-term Gaussian approximation to the scattering factors (Forsyth & Wells, 1959) was used for the structure-factor calculation. The scattering factors approximated were Cu (Viervoll & Øgrim, 1949), I (James & Brindley, 1931) and O (Berghuis *et al.*, 1955). The final R-factor for the nonzero reflections, listed in Table 2, is 0·098. The final parameters, with their standard deviations, are listed in Table 1.

Discussion of the structure

Projections of the structure of salesite on (001) and (010) are shown in Figs. 1 and 2 respectively. The bond distances and angles are listed in Table 3.

The copper atom has the usual square planar coordination with Cu–(OH) 1·95 Å (×2) and Cu–O_2 2·01 Å (×2). Two further oxygen atoms (Cu–O_1 2·59 Å (×2)) complete a distorted octahedron. These octahedra share the bipyramidal edge (OH–O_1) to

Table 1. *Atomic parameters of Salesite*, $CuIO_3(OH)$

	x	y	z	B (Å^2)
Cu	0	0	0	1·16 ± 0·68
I	0·2443 ± 0·00022	$\frac{1}{4}$	−0·006 ± 0·0017	0·67 ± 0·03
(OH)	0·029 ± 0·0027	$\frac{1}{4}$	−0·195 ± 0·0124	0·72 ± 0·23
O_1	0·388 ± 0·0031	$\frac{1}{4}$	0·174 ± 0·0179	1·41 ± 0·23
O_2	0·166 ± 0·0018	0·049 ± 0·0054	0·178 ± 0·0055	0·05 ± 0·25

Table 2. *Observed and calculated structure factors of salesite*, $CuIO_3(OH)$

h	k	l	F_o	F_c
0	2	0	85·5	−97·5
0	4	0	232·0	244·5
0	6	0	79·7	−75·9
0	8	0	126·1	111·1
0	10	0	55·9	−56·4
2	0	0	59·9	−86·2
2	2	0	185·6	225·8
2	3	0	36·0	20·0
2	4	0	66·0	−49·4
2	5	0	30·3	17·3
2	6	0	139·9	139·5
2	8	0	38·5	−36·4
2	10	0	81·4	77·1
4	0	0	178·6	237·4
4	1	0	25·1	−23·5
4	2	0	86·3	−75·9
4	4	0	177·4	178·0
4	5	0	36·9	−25·0
4	6	0	53·3	−49·8
4	8	0	117·5	106·3
4	12	0	56·7	56·3
6	0	0	30·7	−35·7
6	1	0	58·7	57·3
6	2	0	206·9	212·4
6	3	0	61·8	−47·3
6	4	0	54·7	−47·3
6	5	0	35·6	35·6
6	6	0	144·0	120·6
6	8	0	47·2	−50·2
6	10	0	52·5	56·9
8	0	0	169·8	173·5
8	2	0	65·7	−68·1
8	3	0	32·6	26·6
8	4	0	134·3	142·1
8	6	0	48·5	−48·8
8	8	0	92·7	90·7
8	10	0	17·2	−28·8
8	12	0	44·7	49·4
10	0	0	61·3	−52·9
10	3	0	43·7	−43·4
10	4	0	42·3	−45·2
10	6	0	110·7	93·9
10	7	0	33·8	−32·2
10	10	0	65·9	58·4
12	0	0	141·2	116·3
12	1	0	38·8	−33·6
12	2	0	22·8	−24·2
12	3	0	27·1	30·8
12	4	0	96·9	92·0
12	5	0	29·4	−27·3
12	6	0	30·8	−32·7
12	8	0	54·7	49·6
14	0	0	56·2	−49·1
14	1	0	43·2	42·0
14	2	0	109·2	88·4
14	3	0	29·9	−28·8
14	4	0	37·7	−41·3
14	5	0	35·6	41·0
14	6	0	69·7	70·4
14	10	0	51·7	46·8
16	0	0	74·1	60·5
16	1	0	31·5	−30·6
16	2	0	32·3	−30·5
16	4	0	65·4	55·5
16	5	0	29·6	−31·8
16	8	0	54·5	43·1
18	1	0	29·8	27·2
18	2	0	67·8	61·0
18	6	0	48·1	39·1
1	0	1	119·0	121·7
3	0	1	84·6	72·1
4	0	1	57·1	−42·5
5	0	1	127·4	123·4
7	0	1	50·1	37·7
9	0	1	77·0	72·5
10	0	1	26·9	−24·9
13	0	1	68·4	66·9
17	0	1	45·5	46·2
0	0	2	181·8	201·5
1	0	2	30·8	−18·8
2	0	2	77·0	−76·0
4	0	2	219·0	220·6
5	0	2	33·0	−36·4
6	0	2	77·1	−69·6
8	0	2	162·0	152·2
10	0	2	46·0	−42·7
12	0	2	104·1	99·8
16	0	2	72·0	70·0
1	0	3	53·0	60·8
3	0	3	67·2	53·9
5	0	3	54·9	53·4
7	0	3	23·0	14·6
9	0	3	91·3	86·1
13	0	3	49·0	47·6
17	0	3	40·4	41·2
0	0	4	153·3	153·5
2	0	4	50·7	−51·0
4	0	4	143·8	150·6
6	0	4	47·7	−51·3
8	0	4	113·9	114·3
10	0	4	39·7	−40·4
12	0	4	70·2	78·4
16	0	4	55·9	52·8
1	0	5	44·0	50·3
3	0	5	25·9	25·5
5	0	5	56·5	59·2
7	0	5	26·2	15·9
9	0	5	36·0	34·6
13	0	5	40·9	42·5
0	0	6	107·7	117·9
2	0	6	40·1	−45·7
4	0	6	72·8	86·8
6	0	6	33·7	−29·7
8	0	6	67·1	75·3
10	0	6	41·6	−35·6
12	0	6	51·7	63·5
14	0	6	34·0	−30·2
0	0	8	43·0	46·7
0	0	10	37·4	39·3

form zigzag chains parallel to *b*. This type of a chain is known to occur in $Cu_2(OH)_3Br$ (Aebi, 1948), $Cu_2(OH)_3Cl$ (Voronova & Vainshtein, 1958), $Cu_2(OH)_3NO_3$ (Nowacki & Scheidegger, 1952) and $Cu_4(OH)_6SO_4$, brochantite (Cocco & Mazzi, 1959). However, in these structures, the above-mentioned chain joins with another type of copper octahedral chain, formed by sharing the square edges, to form sheets.

Two corners of the pyramidal iodate group share two corners of copper square co-ordination planes, belonging to two octahedra in a chain; the third corner is sharing the apex of an octahedron belonging to the next octahedral chain, displaced from the first by $\frac{1}{2}a$ and $\frac{1}{2}c$. Thus, the iodate groups join the copper octahedral chains in a three-dimensional network. The apices of the pyramidal iodate groups point up and down alternately on either side of the octahedral chain (Fig. 2).

The dimensions of the iodate group are comparable to those found in $Ce(IO_3)_4$ (Cromer & Larson, 1956), $Zr(IO_3)_4$ (Larson & Cromer, 1961), $Ce(IO_3)_4.H_2O$ and other iodates (Ibers, 1956). The $I–O_1$ bond distance is 1·78 Å and the two $I–O_2$ bond distances are 1·82 Å (×2). Though the shortening of the $I–O_1$ bond distance is within the standard deviation and is not statistically significant, similar observations have been made in all the three iodates mentioned above. The apparently short $I–O_1$ distance involves the oxygen, which is not covalently bonded to copper. The average O–I–O angle is 96·7°, as compared to 97·3° in $Ce(IO_3)_4$, 97·1° in $Ce(IO_3)_4.H_2O$ and 94·8° in $Zr(IO_3)_4$. The shortest non-bonded iodine–oxygen distance, I–(OH) is 2·50 Å. The (OH) ion receives a charge contribution of 2/3 from two copper atoms. It is possible that (OH) receives some charge contribution also from the iodine atom. The six nearest oxygen neighbors of the iodine atom form a distorted octahedron, similar to that found in HIO_3 and $Ce(IO_3)_4.H_2O$.

The refractive indices and pleochroism are explained readily by the structure, since the base of the iodate group is nearly parallel to *ab* and the square copper-co-ordination plane makes an angle of about 25° to *ab*.

The perfect (101) cleavage breaks through the long $Cu–O_1$ bond only.

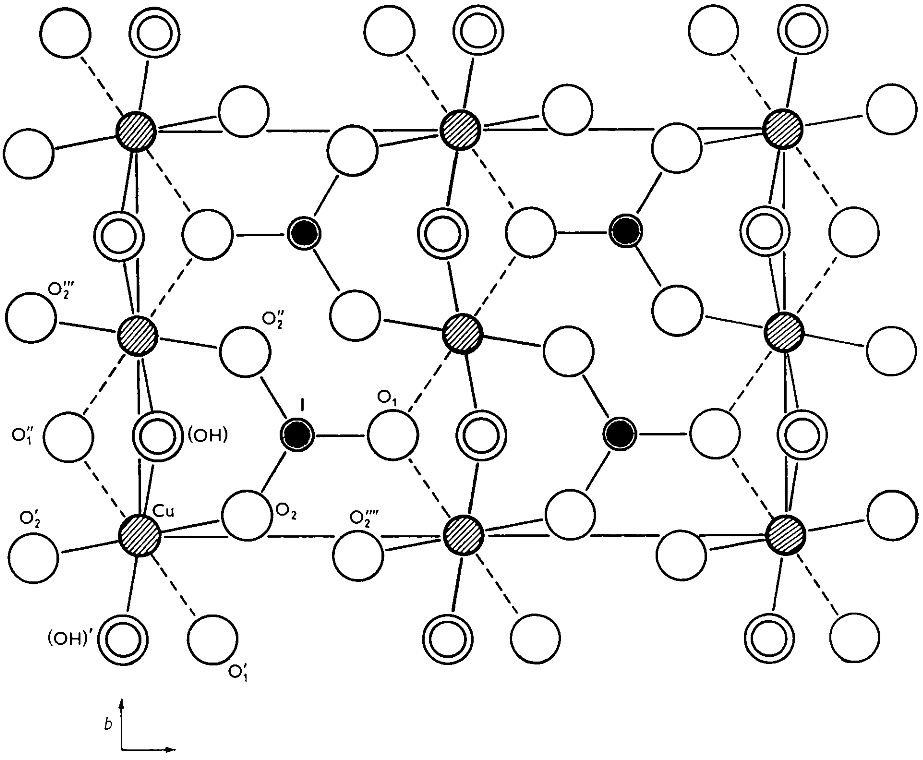

Fig. 1. Projection of the structure of salesite, $CuIO_3(OH)$ on (001).

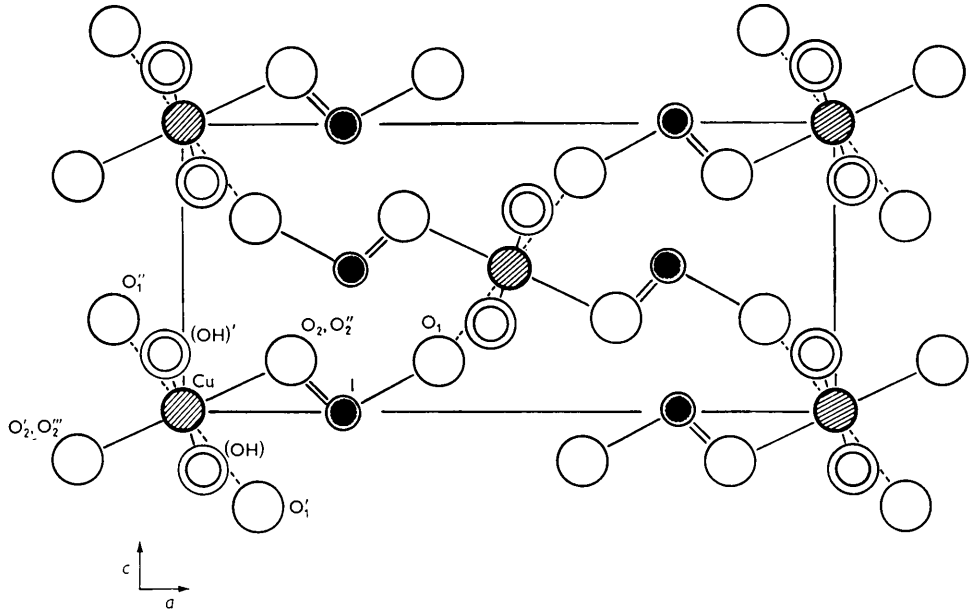

Fig. 2. Projection of the structure of salesite, $CuIO_3(OH)$ on (010).

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Table 3. *Interatomic distances and angles in salesite,* $CuIO_3(OH)$

Within the iodate group		
I–O_1	1·78 ± 0·09 Å	
I–O_2	1·82 ± 0·05	(× 2)
O_1–O_2	2·75 ± 0·10	(× 2)
O_2–O_2''	2·70 ± 0·07	
O_1–I–O_2	97·2 ± 2·1°	(× 2)
O_2–I–O_2''	95·6 ± 1·4	
O_1–O_2–O_2''	60·7 ± 1·5	(× 2)
O_2–O_1–O_2''	58·7 ± 1·5	
Within the copper octahedron		
Cu–(OH)	1·95 ± 0·07 Å	(× 2)
Cu–O_2	2·01 ± 0·05	(× 2)
Cu–O_1'	2·59 ± 0·09	(× 2)
O_2–(OH)	2·68 ± 0·09	(× 2)
O_2–(OH)′	2·91 ± 0·09	(× 2)
O_1'–O_2'	3·37 ± 0·10	(× 2)
O_1'–O_2	3·16 ± 0·10	(× 2)
O_1'–(OH)′	2·75 ± 0·11	(× 2)
O_1'–(OH)	3·53 ± 0·11	(× 2)
(OH)–Cu–O_2	82·5 ± 1·5°	(× 2)
(OH)′–Cu–O_2	97·5 ± 1·5	(× 2)
O_1'–Cu–O_2	84·6 ± 1·6	(× 2)
O_1'–Cu–O_2'	95·4 ± 1·6	(× 2)
O_1'–Cu–(OH)	101·3 ± 1·8	(× 2)
O_1'–Cu–(OH)′	78·7 ± 1·8	(× 2)
Non-bonded I–O distances		
I–(OH)	2·50 ± 0·07 Å	
I–O_2''''	2·69 ± 0·05	

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Stacking Fault in Precipitated Cadmium Sulphide

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In order to throw light upon the nature of stacking fault in precipitated cadmium sulphide, the crystals precipitated in epitaxial orientation on to the galena cleavage face are investigated by means of the electron diffraction reflexion method. It was reported already (Sato, 1959) that the structure of the precipitate is determined mainly by the composition of the aqueous solution of cadmium salt, from which the crystal is precipitated. In the present study, intensity distributions in diffraction patterns of many precipitates obtained with various cadmium salt solutions are dealt with in detail. The conclusions are (1) that the stacking faults observed in precipitated cadmium sulphide are 'growth faults', (2) that the 'Reichweite' of the growth necessary and sufficient for interpretation of the experimental results is 3, and (3) that the 'growth faults' in precipitated cadmium sulphide arise invariably in such a way that the faulty sequences, hex. → cub. and cub. → hex., are comparatively rare.

1. Introduction

In the course of electron diffraction investigations of metathetical actions of a number of aqueous solutions of heavy metal salts upon a number of sulphide mineral surfaces (Sato, 1953*a*, *b*, 1954, 1955, 1957), cadmium sulphide in epitaxial orientation has been obtained on the cleavage face of galena (PbS; NaCl-type cubic) treated with cadmium salt solutions. The function of galena in this surface reaction lies, first, in supplying