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Salesite, $CuIO_3(OH)$, and $Cu(IO_3)_2 \cdot 2H_2O$: a comparison of the crystal structures and their magnetic behavior[1]

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Abstract

The structurally closely-related compounds $Cu(IO_3)_2 \cdot 2H_2O$ and salesite, $Cu(IO_3)(OH)$, are monoclinic and orthorhombic respectively, with cell dimensions $a = 6.728(1)$, $b = 4.813(1)$, $c = 11.165(2)$A, $\beta = 103.34(1)°$; space group $P2_1/c$, $Z = 2$; and $a = 10.794(2)$, $b = 6.708(1)$, $c = 4.781(1)$A, space group *Pnma*, $Z = 4$. The crystal structure of $Cu(IO_3)_2 \cdot 2H_2O$ has been determined by the heavy-atom method. The crystal structures of both compounds have been refined by the method of least squares to *R* factors of 0.026 and 0.031, based on 1284 and 715 reflections measured on an automatic single-crystal diffractometer. The hydrogen positions have been determined for both phases.

The $[CuO_4(H_2O)_2]$ octahedron in $Cu(IO_3)_2 \cdot 2H_2O$ and the $[CuO_4(OH)_2]$ octahedron in salesite are tetragonally distorted, with the water molecules and the (OH) ions in each structure occurring in a *trans*-configuration within the square plane. The four square planar Cu–O bonds average 1.953 and 1.968A, and two axial Cu–O bonds average 2.457 and 2.538A in $Cu(IO_3)_2 \cdot 2H_2O$ and salesite respectively. The $[IO_3]$ groups in both structures are trigonal pyramids, deviating significantly from the highest possible point-group symmetry *3m*. The three short I–O bonds average 1.811 and 1.824A, and the O–I–O angles 99.7 and 97.9°; three additional long I–O bonds average 2.815 and 2.637A within the distorted octahedral $[IO_5(H_2O)]$ and $[IO_5(OH)]$ groups in the structures of $Cu(IO_3)_2 \cdot 2H_2O$ and salesite respectively. Both structures consist of corner-sharing I-octahedra forming an open sheet structure, which are cross-linked by Cu-octahedra. In $Cu(IO_3)_2 \cdot 2H_2O$, the Cu-octahedra are isolated, whereas in salesite they share edges to form infinite chains parallel to the *b* axis. The hydrogen atoms in both structures are involved in hydrogen bonding.

$Cu(IO_3)_2 \cdot 2H_2O$ is paramagnetic down to 1.4 K, whereas salesite may be anti-ferromagnetic below 162 K. The different magnetic behavior in these two phases is explained by the fact that the Cu–Cu separation is 6.508A in $Cu(IO_3)_2 \cdot 2H_2O$ and 3.354A within the octahedral chain in salesite. A model is proposed of the magnetic structure of salesite with the magnetic spins alternately up and down, either parallel or normal to the *b* axis.

Introduction

Of the two known mineral iodates of copper, salesite, $CuIO_3(OH)$, was described by Palache and Jarrell (1939), and bellingerite, $3Cu(IO_3)_2 \cdot 2H_2O$, by Berman and Wolfe (1940). The crystal structure of salesite was determined by Ghose (1962) and of bellingerite by Ghose and Wan (1974). Both these minerals were synthesized by Granger and de Schulten (1904). Salesite, bellingerite, and four new copper iodates have been synthesized by Nassau *et al.* (1973) by the gel-growth technique. Their crystallographic, magnetic, and optical properties were determined by Abrahams *et al.* (1973b). Of these four new copper iodate phases, three are anhydrous $Cu(IO_3)_2$ and the fourth is hydrated, namely $Cu(IO_3)_2 \cdot 2H_2O$. This hydrated phase is monoclinic, with cell dimensions very similar to those of salesite, which is orthorhombic. This fact suggested that these two structures may be closely comparable. This is indeed the case, as shown by the structure determination of $Cu(IO_3)_2 \cdot 2H_2O$ reported in this paper. In this connection, the structure of salesite (Ghose, 1962) has been refined using three-dimensional intensity data. In spite of the structural similarity, the magnetic properties of these two

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phases are quite different. While $Cu(IO_3)_2 \cdot 2H_2O$ remains paramagnetic down to 1.4K, $CuIO_3(OH)$ shows possible antiferromagnetic ordering at 162K (Abrahams *et al.*, 1973b). This difference in magnetic behavior is discussed in terms of the structures of these two phases.

Crystal data

Unit-cell dimensions of salesite and $Cu(IO_3)_2 \cdot 2H_2O$ were determined by the least-squares refinement of 15 reflections each, with 2θ values between 35 and 45° measured with Mo$K\alpha$ radiation on an automatic single-crystal diffractometer (Table 1). They are in good agreement, within error limits, with those reported by Abrahams *et al.* (1973b).

Table 1. Crystal data: $Cu(IO_3)_2 \cdot 2H_2O$ and salesite, $CuIO_3(OH)$ (standard deviations in parentheses)

$Cu(IO_3)_2 \cdot 2H_2O$		Salesite $CuIO_3(OH)$ (Chuquicamata, Chile)	
a (Å)	6.7280(12)	a (Å)	10.7935(17)Å
b (Å)	4.8132(9)	b (Å)	6.7075(13)
c (Å)	11.1646(16)	c (Å)	4.7813(9)
β (°)	103.34(1)	β (°)	90.0
Cell volume ($Å^3$):	351.79(11)	Cell volume ($Å^3$):	346.15(12)
Space group:	$P2_1/c$	Space group:	$Pnma$
Cell content:	$2[Cu(IO_3)_2 \cdot 2H_2O]$	Cell content:	$4[CuIO_3(OH)]$
D_m ($g.cm^{-3}$):		D_m ($g.cm^{-3}$):	4.77
D_c ($g.cm^{-3}$):	4.289	D_c ($g.cm^{-3}$):	4.900
μ(MoKα) (cm^{-1}):	121.26	μ(MoKα) (cm^{-1}):	155.44

Collection of intensity data

Small spheres of $CuIO_3(OH)$ and $Cu(IO_3)_2 \cdot 2H_2O$ with diameters 0.22 and 0.20 mm respectively were prepared. All reflections within $2\theta = 65°$ were measured on a single-crystal automatic diffractometer (Syntex $P\bar{1}$), using Mo$K\alpha$ radiation, monochromatized by reflection from a graphite "single" crystal and a scintillation counter. A variable scan rate was used in both cases, the minimum being 1°/min., and the maximum 24°/min. (50 kV, 12.5 mA). For reflections with intensities less than $0.7\sigma(I)$, where $\sigma(I)$ is the standard error of measurement derived from the counting statistics, I was set equal to $0.7\sigma(I)$, regardless of whether measured I was positive or negative. A total of 1284 reflections were measured for $Cu(IO_3)_2 \cdot 2H_2O$ and 715 for $CuIO_3(OH)$. The measured intensities were corrected for Lorentz, polarization, and absorption factors. No corrections were made for extinction effects.

Determination and refinement of the structures

$Cu(IO_3)_2 \cdot 2H_2O$

The cell content and the space group of $Cu(IO_3)_2 \cdot 2H_2O$, $P2_1/c$ require that the Cu atoms be

Table 2. $Cu(IO_3)_2 \cdot 2H_2O$ and salesite, $CuIO_3(OH)$: atomic positional and thermal parameters (standard deviations in parentheses)

	x	y	z	B eq.*	β_{11}†	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
				$Cu(IO_3)_2 \cdot 2H_2O$						
Cu	0	0	0	0.94(1)	40(1)	136(3)	18(1)	0(1)	5(1)	13(1)
I	0.26058(3)	0.36380(5)	0.26659(2)	0.72(1)	32(1)	113(1)	12(1)	-4(1)	4(1)	3(1)
O(1)	0.4765(4)	0.1552(7)	0.3407(3)	1.47(5)	51(5)	209(13)	31(2)	28(6)	-2(3)	9(4)
O(2)	0.0705(4)	0.1995(6)	0.3364(3)	1.20(4)	55(5)	171(11)	25(2)	-21(6)	15(3)	6(4)
O(3)	0.2101(5)	0.2078(7)	0.1151(3)	1.37(4)	71(5)	233(13)	15(2)	-31(7)	5(3)	-27(4)
O(W	0.7791(4)	0.2329(6)	0.0311(3)	1.23(4)	70(5)	148(11)	22(2)	25(7)	4(3)	-7(4)
H(1)	0.821(8)	0.383(11)	0.073(5)	0.8(9)						
H(2)	0.655(13)	0.279(18)	-0.041(8)	2.0(1.7)						
				Salesite, $CuIO_3(OH)$						
Cu	0	0	0	1.06(1)	21(1)	52(1)	142(2)	-8(1)	-12(1)	20(2)
I	0.24486(2)	0.25	-0.00005(11)	0.79(1)	15(1)	40(1)	102(1)	0	-1(1)	0
O(1)	0.3866(4)	0.25	0.1947(11)	1.54(7)	21(3)	106(9)	187(18)	0	-19(6)	0
O(2)	0.1624(3)	0.0482(4)	0.1829(7)	1.15(4)	24(2)	54(4)	150(10)	-8(3)	-14(4)	30(7)
(OH)	0.0295(4)	0.25	-0.1967(10)	0.98(5)	24(2)	42(6)	119(13)	0	2(1)	0
H	0.026(11)	0.25	-0.394(31)	6.0(3.3)						

*Equivalent isotropic temperature factor, calculated from anisotropic temperature factors.

†Form of the anisotropic temperature factor (x10^4): $-exp\ \{\sum_{i=1}^{3}\sum_{j=1}^{3} h_i h_j \beta_{ij}\}$

Table 4. $Cu(IO_3)_2 \cdot 2H_2O$ and salesite, $CuIO_3(OH)$: interatomic distances (A) and angles (°) (standard deviations in parentheses)

	$Cu(IO_3)_2 \cdot 2H_2O$		
	The Cu-Octahedron		
Cu-O(2)	2.457(3) (x2)	O(2)-Cu-O(3)	87.2(1) (x2)
Cu-O(3)	1.951(3) (x2)	O(2)-Cu-O(W)	94.5(1) (x2)
Cu-O(W)	1.955(3) (x2)	O(2)-Cu-O(3')	92.8(1) (x2)
Mean of		O(2)-Cu-O(W')	85.5(1) (x2)
nearest 4	1.953	O(3)-Cu-O(W)	93.1(1) (x2)
Mean of 6	2.121	O(4)-Cu-O(3')	86.9(1) (x2)
O(2)-O(3)	3.063(4) (x2)		
O(2)-O(W)	3.259(4) (x2)		
O(2)-O(3')	3.211(4) (x2)		
O(2)-O(4')	3.017(4) (x2)		
O(3)-O(W)	2.837(4) (x2)		
O(4)-O(3')	2.686(4) (x2)		
Mean	3.012		
	The I-Polyhedron		
I-O(1)	1.802(3)	O(1)-I-O(2)	97.7(1)
I-O(2)	1.824(3)	O(2)-I-O(3)	102.7(1)
I-O(3)	1.807(3)	O(3)-I-O(1)	98.9(2)
Mean of 3	1.811	Mean	99.7
I-O(1')	2.739(3)		
I-O(2')	2.777(3)		
I-O(W')	2.930(3)		
I-O (mean of 6)	2.313		
	Hydrogen bonds		
H(1)-O(W)	0.87(6)	H(1)-O(W)-H(2)	110(6)
H(1)-O(2")	1.88(6)	O(4)-H(1)-O(2')	176(5)
O(W)-O(2")	2.749(4)	H(1)-O(4)-Cu	114(4)
H(2)-O(W)	1.04(9)	H(1)-O(4)-I	99(4)
H(2)-O(1')	1.60(9)	O(4)-H(2)-O(1")	176(8)
O(W)-O(1')	2.635(4)	H(2)-O(4)-Cu	119(5)
		H(2)-O(4)-I	122(5)
	Salesite, $CuIO_3(OH)$		
	The Cu-Octahedron		
Cu-O(1)	2.538(3) (x2)	O(1)-Cu-O(2)	86.3(1) (x2)
Cu-O(2)	1.986(3) (x2)	O(1)-Cu-O(2')	93.7(1) (x2)
Cu-(OH)	1.949(2) (x2)	O(1)-Cu-(OH)	102.3(1) (x2)
Mean of		O(1)-Cu-(OH)'	77.8(1) (x2)
nearest 4	1.968	O(2)-Cu-(OH)	85.9(2) (x2)
Mean of 6	2.158	O(2)-Cu-(OH)'	94.1(2) (x2)
		Mean	90.0
O(1)-O(2)	2.773(4) (x2)		
O(1)-O(2')	3.120(5) (x2)		
O(1)-(OH)	3.514(7) (x2)		
O(1)-(OH)'	2.853(7) (x2)		
O(2)-(OH)	2.680(5) (x2)		
O(2)-(OH)'	2.880(4) (x2)		
Mean	2.970		
Cu-Cu	3.354(1)		
Cu-I	3.130(1)		
	The I-Polyhedron		
I-O(1)	1.791(4)	O(1)-I-O(2)	99.6(2) (x2)
I-O(2)	1.840(3) (x2)	O(2)-I-O(2')	94.7(2)
Mean	1.824	Mean	97.9
O(1)-O(2)	2.773(4) (x2)		
O(2)-O(2")	2.707(6)		
Mean	2.751		
I-(OH)	2.507(4)		
I-O(2)	2.702(3) (x2)		
I-O (mean of 6)	2.231		
	Hydrogen bond		
H-(OH)	0.94(2)	(OH)-H...O(1)	135.7(10.0)
H-O(1)	2.08(1)	H-(OH)-Cu	118.5(1.5)
(OH)-O(1)	2.837(7)		

in a two-fold special position, which were assigned to (0,0,0) and (0,1/2,1/2). The positions of four equivalent iodine atoms were determined from the three-dimensional Patterson synthesis. A refinement of the structure with contributions from Cu and I atoms yielded an R factor of 0.15. A difference Fourier synthesis indicated the positions of four different oxygen atoms. Inclusion of these oxygen positions in the refinement of the structure, using isotropic temperature factors, reduced the R factor to 0.069.

Two cycles of least-squares refinement of the structure, using anisotropic temperature factors based on all non-hydrogen atoms, yielded an R factor of 0.026. A difference Fourier synthesis calculated at this stage clearly showed the positions of the two different hydrogen atoms. Two cycles of refinement using anisotropic temperature factors for all atoms, except hydrogens for which isotropic temperature factors were used, yielded an R factor of 0.025 for 1284 reflections.

$CuIO_3(OH)$

A structure factor calculation for $CuIO_3(OH)$ based on the atomic coordinates of Ghose (1962) yielded an R factor of 0.091 for 715 reflections. Eight lower-angle reflections showed large differences between observed and calculated structure factors. These reflections were believed to be affected by extinction and were excluded from the refinement. Three cycles of refinement using anisotropic temperature factors for Cu, I, and O yielded an R factor of 0.028. A difference Fourier synthesis calculated at this stage showed the hydrogen position clearly. However, attempts to refine the hydrogen position using isotropic temperature factors failed because of an interaction of the temperature factor with the z parameter. The refinement was terminated when the R factor for 707 unrejected reflections showed a minimum value of 0.026. The R factor for all reflections at this stage was 0.031. The hydrogen position is tentative in view of the lack of refinement.

For the refinement of both structures, scattering factors for Cu, I, O, and H were taken from Cromer and Mann (1968). Anomalous dispersion corrections were made according to Cromer and Liberman (1970). The full-matrix least-squares program RFINE (Finger, 1969) was used for the refinement of both structures. The observed structure factors (F_o's) were weighted according to the formula $F_o/\sigma^2(F_o)$, where $\sigma(F_o)$ is the standard deviation in the measurement of F_o, as derived from the counting statistics. The atomic parameters for both phases are listed in Table

2, and the observed and calculated structure factors in Table 3.[2] Table 4 lists the bond lengths and angles, and Table 5 lists the ellipsoids of thermal vibration. The average standard deviations in Cu–O, I–O, and O–H bond lengths in both structures are 0.003, 0.003, and 0.06A and in O–Cu–O, O–I–O, and H–O–H angles 0.1, 0.1, and 6.0° respectively.

Description of the structures

$Cu(IO_3)_2 \cdot 2H_2O$

The structure of $Cu(IO_3)_2 \cdot 2H_2O$ consists of corner-sharing $[CuO_4(H_2O)_2]$ octahedra and trigonal pyramidal $[IO_3]$ groups.

Stereochemistry of the cupric ion. The isolated $[CuO_4(H_2O)_2]$ octahedron is in fact a tetragonal bipyramid and shows the usual Jahn-Teller type distortion (Fig. 1). Two oxygen atoms and two water molecules form a square plane around the copper atom [Cu–O 1.951 and Cu–O(W) 1.955A], while two further oxygen atoms (Cu–O 2.457A) complete the octahedron. The Cu octahedron has the point-group symmetry $\bar{1}$. The water molecules occur in *trans*-configuration within the square plane. The Cu–O–H angles are 114 and 119°.

Stereochemistry of the iodine (V) ion. The iodine atom is closely bonded to three oxygen atoms at distances of 1.802, 1.824, and 1.807A (Fig. 1). The $[IO_3]$ group is a trigonal pyramid, with O–I–O angles of 97.7, 102.7, and 98.9°. It deviates slightly but significantly from the highest possible point-group symmetry *3m*. The iodine atom is further bonded to two oxygen atoms and a water molecule at distances of 2.739, 2.777, and 2.930A respectively. The $[IO_5(H_2O)]$ polyhedron can be described as a highly distorted octahedron or a trigonal anti-prism (Fig. 3a).

Configuration of the H_2O molecule and hydrogen bonding. The water molecule forms a common corner of both the Cu- and I-octahedra. The O–H distances are 0.87 and 1.04A, and the H–O–H angle is 110°, which is well within the limit of 102.5–115.5° found in crystalline hydrates (Falk and Knop, 1973). H(1) is hydrogen bonded to O(2″), which is bridging the Cu- and I-octahedra. The H(1)···O(2″) distance is 1.88A, and the O(W)–H(1)···O(2″) angle is 176° (Fig. 1). H(2) is hydrogen bonded to O(1″), which is a non-bridging corner of the iodine-polyhedron. The H(2)···O(1″) distance is 2.04A, and the O(W)–H(2)–O(1″) angle is 176°. Hence, both hydrogen bonds are nearly straight bonds, deviating very slightly from O(W)–O(2″) and O(W)–O(1″) directions. Although the H–O–H angle is close to the ideal tetrahedral angle, other bonds around O(W), namely O(W)–Cu and O(W)···I deviate considerably from an ideal tetrahedral configuration with respect to the O(W)–H(1) and O(W)–H(2) bonds (Table 3). In fact the H(2)–O(W)–Cu and H(2)–O(W)–I angles are close to being trigonal rather than tetrahedral.

The three-dimensional framework. The $[IO_5(H_2O)]$ polyhedron shares four corners with adjacent I polyhedra. An open polyhedral sheet parallel to the (001) plane is thereby formed (Fig. 3a). Isolated $[CuO_4(H_2O)_2]$ octahedra bind these sheets together in a three-dimensional framework by sharing two sets of octahedral edges with two iodine-polyhedral sheets

Table 5. $Cu(IO_3)_2 \cdot 2H_2O$ and salesite, $CuIO_3(OH)$: ellipsoids of thermal vibration (standard deviations in parentheses)

Atom	Axis, r_i	Root mean square displacement (Å)	Angle (°) with respect to +a	+b	+c
			$Cu(IO_3)_2 \cdot 2H_2O$		
Cu	1	0.093	168(18)	81(9)	69(18)
	2	0.096	116(16)	112(7)	134(12)
	3	0.133	97(1)	31(2)	117(2)
I	1	0.082	148(36)	80(10)	47(33)
	2	0.084	54(36)	88(4)	49(36)
	3	0.116	86(1)	7(1)	97(1)
O(1)	1	0.093	160(6)	109(6)	71(6)
	2	0.146	115(14)	91(12)	142(14)
	3	0.161	105(12)	15(12)	86(14)
O(2)	1	0.092	135(10)	74(6)	118(8)
	2	0.125	61(24)	90(16)	164(24)
	3	0.147	72(8)	24(10)	79(7)
O(3)	1	0.078	98(6)	69(3)	22(4)
	2	0.124	35(7)	98(5)	69(7)
	3	0.175	77(4)	18(4)	105(3)
O(W)	1	0.110	142(195)	126(198)	87(158)
	2	0.112	91(124)	111(101)	154(12)
	3	0.148	124(10)	49(8)	111(8)
			$CuIO_3(OH)$		
Cu	1	0.095	129(9)	40(9)	94(5)
	2	0.105	51(7)	63(5)	130(6)
	3	0.142	63(3)	63(3)	40(2)
I	1	0.095	176(19)	90	86(19)
	2	0.095	90	180	90
	3	0.109	86(4)	90	4(4)
O(1)	1	0.101	156(17)	90	66(17)
	2	0.155	114(273)	90	156(273)
	3	0.156	90	0	90
O(2)	1	0.096	100(20)	29(16)	117(10)
	2	0.108	30(33)	95(30)	119(34)
	3	0.151	62(7)	61(7)	42(4)
(OH)	1	0.098	90	0	90
	2	0.115	131(99)	90	138(99)
	3	0.120	138(101)	90	49(101)

[2] To obtain a copy of Table 3, order document AM-77-061 from the Business Office, Mineralogical Society of America, 1909 K Street, N.W., Washington, D.C. 20006. Please remit $1.00 in advance for the microfiche.

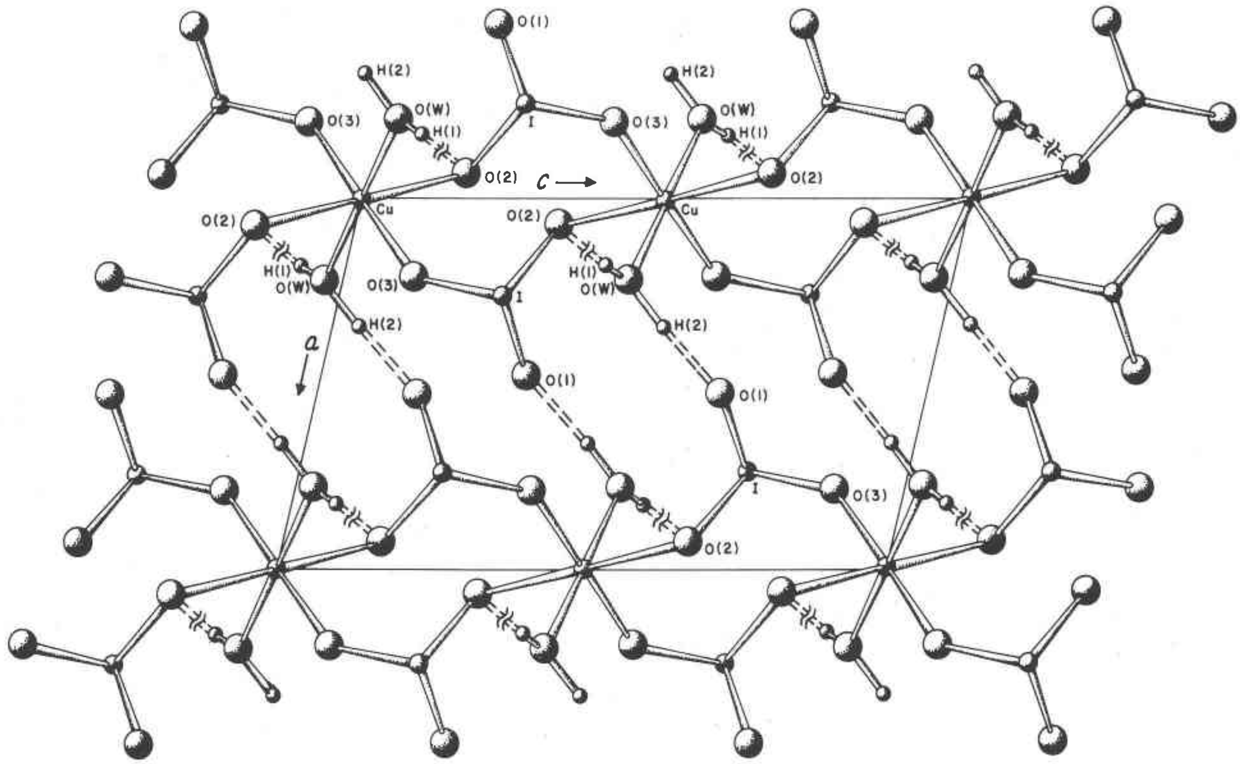

Fig. 1. A view of the $Cu(IO_3)_2 \cdot 2H_2O$ structure down the *b* axis. Note the hydrogen bonds (shown by broken lines).

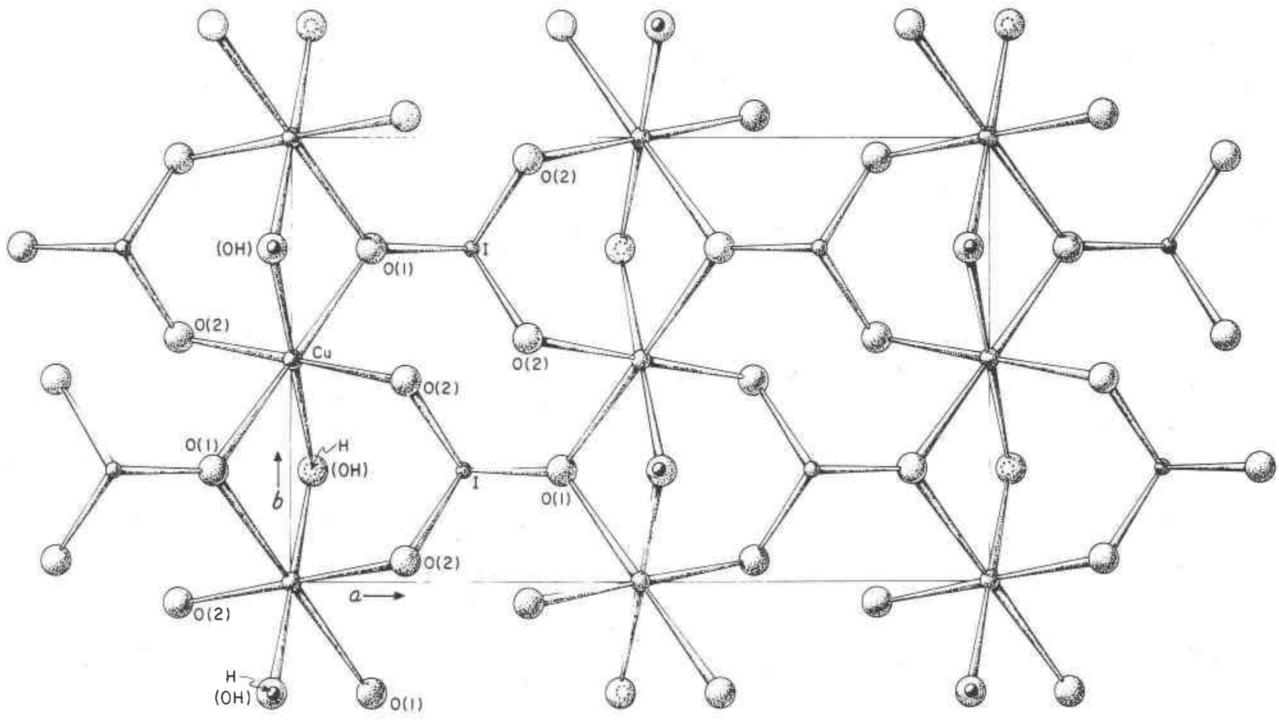

Fig. 2. A view of salesite, $CuIO_3(OH)$ structure, down the *c* axis.

on either side. One of the hydrogen bonds [O(W)–H(1)···O(2″)] binds two isolated Cu octahedra together, whereas the other [O(W)–H(2)–O(1″)] binds a Cu octahedron to an I polyhedron.

Salesite, $CuIO_3(OH)$

The structure of salesite consists of chains of edge-sharing [$CuO_4(OH)_2$] octahedra and corner-sharing trigonal pyramidal [IO_3] groups (Ghose, 1962).

Stereochemistry of the cupric ion. The [$CuO_4(OH)_2$] polyhedron is a tetragonal bipyramid with the point group symmetry $\bar{1}$. Two oxygen atoms and two (OH) ions form a square plane around the Cu atom [Cu–O 1.986A, Cu–(OH) 1.949A]; two further oxygen atoms (Cu–O 2.538A) complete the bipyramid. The (OH) ions occur in a *trans*-configuration within the square plane.

Stereochemistry of the iodine (V) ion. The iodine atom is closely bonded to three oxygen atoms in the form of a trigonal pyramid. The [IO_3] group, with the point group symmetry *m*, deviates significantly from the highest possible symmetry *3m*. Thus, the I–O(1) bond (1.791A) is significantly shorter than the two I–O(2) bonds (1.804A), and one of the O–I–O angles [O(2)–I–O(2′) 94.7°] is significantly smaller than the other two [O(1)–I–O(2) 99.6°]. The iodine atom is further bonded to the (OH) ion at 2.507A and two oxygen atoms at 2.702A. The [$IO_5(OH)$] polyhedron can be described as a highly distorted octahedron or a trigonal antiprism (Fig. 3b).

The weak I–(OH) bond (2.507A) is the shortest extra-pyramidal bond recorded so far, the only other analogous case being $Ce(IO_3)_4 \cdot H_2O$ (Ibers, 1956), where an I–O contact of 2.51A has been reported. The (OH) group is charge-deficient, because it is bonded to two Cu atoms at 2.539A in addition to the H atom at 0.94A. Hence the I–(OH) bond must be significant, albeit weak.

Hydrogen bond. The (OH) group is hydrogen-bonded to O(1″), an oxygen corner belonging to an adjacent Cu-octahedral chain (see below) separated by the *c* dimension. The O–H and H···O distances are 0.94 and 2.08A. The O–H···O angle is 136°. Hence, the hydrogen bond is a strongly-bent bond.

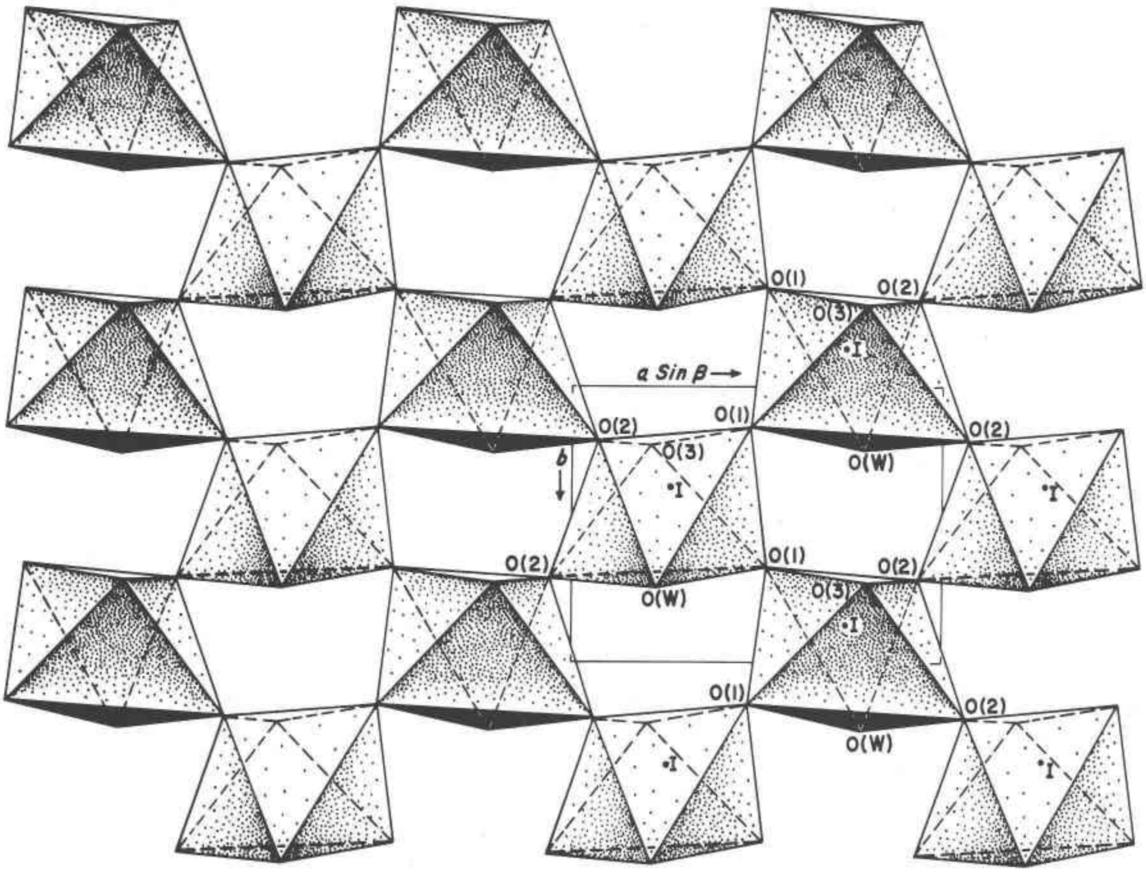

Fig. 3a. Linkage of the I-octahedra in $Cu(IO_3)_2 \cdot 2H_2O$, viewed down the *c* axis.

The three-dimensional framework. The $[IO_5(OH)]$ octahedron shares four oxygen corners with four adjacent I octahedra to form an open octahedral sheet parallel to the (100) plane (Fig. 3b). The $[CuO_4(OH)_2]$ octahedron shares two opposite edges with two adjacent Cu octahedra to form octahedral chains parallel to the *b* axis (Fig. 2). Adjacent Cu-octahedral chains are separated from each other by $1/2\mathbf{a} + 1/2\mathbf{c}$. Each Cu octahedron shares a set of two edges with two sets of I octahedra belonging to the two I-polyhedral sheets occurring on either side of the octahedron. In this fashion, the Cu-octahedral chains and the I-polyhedral sheets are connected together in a three-dimensional framework.

A comparison of the structural schemes of $CuIO_3(OH)$ and $Cu(IO_3)_2 \cdot 2H_2O$

In both structures, the I octahedra share corners to form an open sheet structure (Figs. 3a, b), which are connected by Cu octahedra. In $Cu(IO_3)_2 \cdot 2H_2O$ with the Cu:I ratio 1:2, the $[CuO_4(H_2O)_2]$ octahedron is isolated; in $CuIO_3(OH)$, on the other hand, with Cu:I ratio 1:1, the $[CuO_4(OH)_2]$ octahedra form infinite chains. Topologically, the $Cu(IO_3)_2 \cdot 2H_2O$ structure can be derived from that of $Cu(IO_3)(OH)$, by removing half of the Cu octahedra, specifically those which occur on either side of the Cu octahedron occurring at (0,0,0) (Figs. 1 and 2).

The reason for the deviation from orthorhombic symmetry in $Cu(IO_3)_2 \cdot 2H_2O$ probably lies in the Cu-octahedral edges shared with the I polyhedra; in $CuIO_3(OH)$, the edges of the Cu square plane are shared, whereas in $Cu(IO_3)_2 \cdot 2H_2O$ the bipyramidal edges are shared.

Models of magnetic structures for $Cu(IO_3)_2 \cdot 2H_2O$ and $CuIO_3(OH)$

$Cu(IO_3)_2 \cdot 2H_2O$ is a simple paramagnet down to 1.4 K; its paramagnetic moment of $1.72\mu_B$ is exactly that predicted for spin-only Cu^{2+}. The inverse magnetic susceptibility of salesite shows an inflection at 162 K, which may indicate antiferromagnetic ordering. Its high-temperature paramagnetism, with a Curie constant of 0.62 cm^3 K $mole^{-1}$, corresponds to a

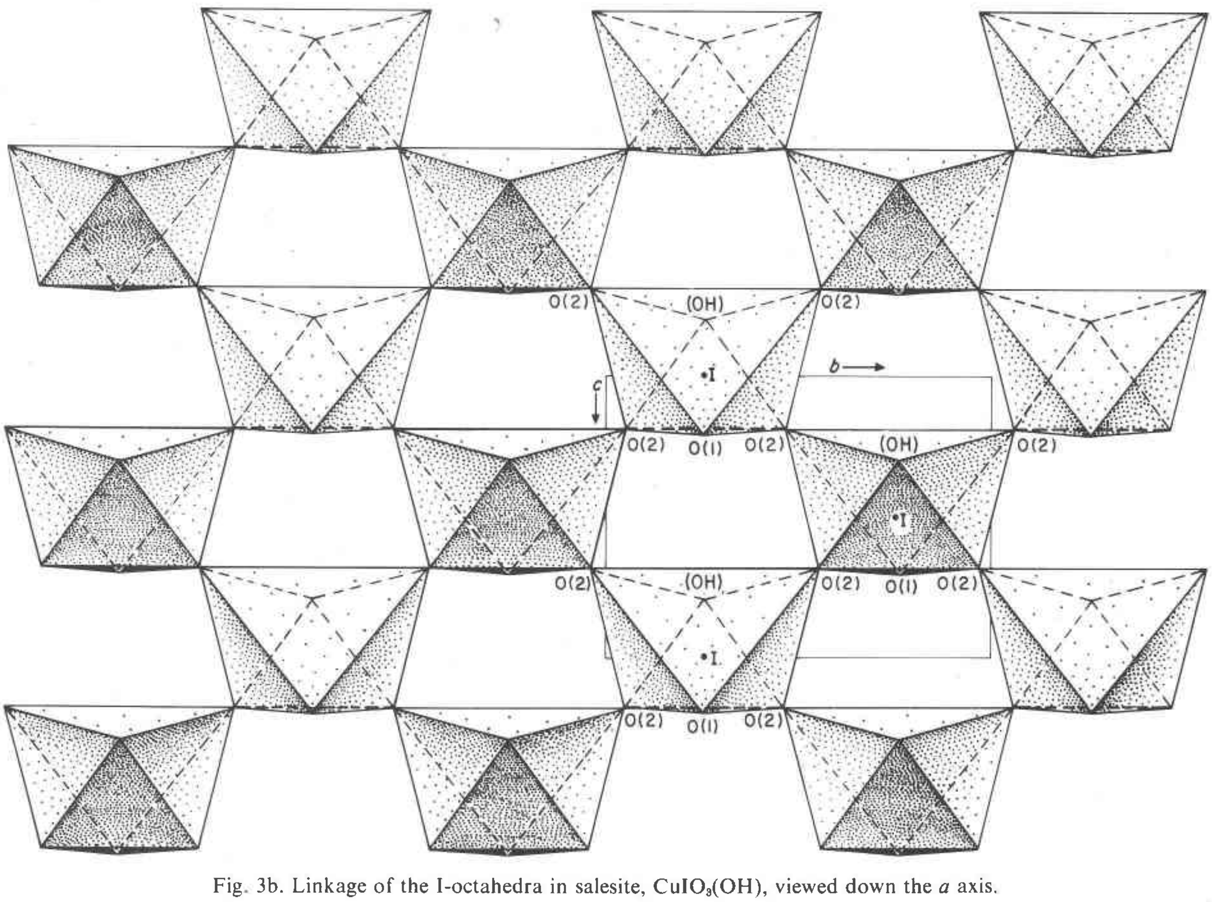

Fig. 3b. Linkage of the I-octahedra in salesite, $CuIO_3(OH)$, viewed down the *a* axis.

moment of $2.23\mu_B$; extrapolation gives a Curie temperature of -340 K, corresponding to very strong antiferromagnetic Cu–Cu interactions (Abrahams *et al.*, 1973b).

In $Cu(IO_3)_2 \cdot 2H_2O$, the Cu atoms occur in isolated octahedra, the nearest Cu–Cu distance being 6.508A. A possible magnetic interaction between two neighboring Cu atoms involves a long super-exchange path: Cu–O(3)–I–O(2)–Cu along [011]. Cu–O(2) is the long (2.46A) bond, where the covalency factor is very small. A larger Cu–Cu separation, along with the long Cu–O bond involved in the exchange path, may account for a lack of magnetic ordering in $Cu(IO_3)_2 \cdot 2H_2O$ down to 1.4 K. It is quite possible, however, that a transition to a magnetically-ordered state exists below this temperature.

$Ni(IO_3)_2 \cdot 2H_2O$, on the other hand, is weakly ferromagnetic below 3 K, which involves interaction between two closest Ni atoms, 5.636A apart, through an exchange path of the type Ni–O–I–O–Ni (Abrahams *et al.*, 1973a).

The situation in $Cu(IO_3)OH$ is quite different, where the Cu atoms occur in octahedral chains parallel to the *b* axis, the Cu–Cu separation within the chain being 3.354A. Of the two short exchange paths, Cu–(OH)–Cu is the shortest, with Cu–(OH) distance 1.949A; the next shortest path is Cu–O(1)–Cu, with Cu–O(1) distance 2.538A. A longer path involves O(2) and I, namely Cu–O(2)–I–O(2)–Cu. The interaction between the neighboring chains of Cu-atoms involves a long exchange path Cu–O(2)–I–O(1)–Cu.

We may conceive of two possible models for antiferromagnetic ordering in $CuIO_3(OH)$: (1) within any single chain the spins are alternately up and down either parallel or normal to the *b* axis; (2) the spins are collinear in each chain, but antiparallel with respect to neighboring chains. In view of the long exchange path involved in terms of two neighboring Cu chains, the first model is to be preferred.

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