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The Crystal Structure and Magnetic Behavior of γ-$Cu(IO_3)_2$

BY RUNE LIMINGA AND SAFIA R. BOOLES*

Institute of Chemistry, University of Uppsala, Box 531, *S*-751 21, *Uppsala, Sweden*

AND SUBRATA GHOSE AND CHE'NG WAN

Department of Geological Sciences, University of Washington, Seattle, WA 98195, *USA*

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γ-$Cu(IO_3)_2$ is monoclinic, space group $P2_1/m$, with cell dimensions, a = 4·9944 (7), b = 6·3810 (6), c = 8·1915 (12) Å, β = 92·08 (1)°, Z = 2. The structure has been determined by the heavy-atom method and refined by the least-squares method to an R value of 0·021 for 2437 reflections measured on an automatic single-crystal diffractometer. The CuO_6 octahedron is tetragonally distorted with four shorter bonds [1·951 (×2) and 2·002 (×2) Å] within the square plane and two longer apical bonds [2·359 (×2) Å]. The average I—O bond lengths (and O—I—O bond angles) within $I(1)O_3$ and $I(2)O_3$ trigonal pyramids are 1·817 Å (99·4°) and 1·825 Å (96·7°) respectively. I(1) is weakly bonded to two further oxygens at a distance of 2·600 Å, the $I(1)O_5$ polyhedron being a distorted trigonal bipyramid. I(2) is further bonded to two oxygen atoms at a distance of 2·637 Å and two at 3·064 Å; the $I(2)O_7$ polyhedron is an irregular polyhedron. The structure of γ-$Cu(IO_3)_2$ consists of $Cu(IO_3)_2$ columns parallel to the b axis, formed by edge-sharing CuO_6 octahedra and edge- and/or corner-sharing $I(1)O_3$ and $I(2)O_3$ groups; these columns are cross linked into a three-dimensional framework through long I—O bonds. γ-$Cu(IO_3)_2$ is antiferromagnetic, with a Néel temperature of 5 K. The paramagnetic Curie temperature is positive, indicating ferromagnetic Cu–Cu interactions [Abrahams, Sherwood, Bernstein & Nassau (1973). *J. Solid State Chem.* **8**, 274–279]. The proposed model for antiferromagnetic ordering calls for spins, which are collinear within each edge-sharing copper-octahedra chain, but antiparallel with respect to neighboring chains.

Introduction

Three anhydrous cupric iodates have been synthesized by the gel growth technique (Nassau, Cooper, Shiever & Prescott, 1973), whose crystallographic, magnetic and non-linear optical properties have been determined by Abrahams, Sherwood, Bernstein & Nassau (1973). Only one of the cupric iodates, α-$Cu(IO_3)_2$, crystallizes in a polar space group. Its crystal structure and the absolute signs of the piezo- and pyroelectric coefficients relative to the absolute atomic arrangements have been determined by Liminga, Abrahams & Bernstein (1975*b*) and Liminga & Abrahams (1976) respectively. In this paper, we report on the crystal structure of the centrosymmetric γ-$Cu(IO_3)_2$ phase, and compare it with those of α-$Cu(IO_3)_2$ and $CuIO_3(OH)$, salesite.

Crystal data

The unit-cell dimensions were determined from powder photographs taken with a Guinier–Hägg XDC-700 camera at 22 °C using Cr $K\alpha$ radiation (λ = 2·28962 Å), with CoP_3 as an internal standard (a = 7·7078 Å). The unit-cell dimensions, derived from a least-squares refinement of the observed 2θ values of 19 reflections, are listed in Table 1.

Table 1. *Crystal data*

γ-$Cu(IO_3)_2$, dark yellow prism
Monoclinic, $2/m$
$a = 4·9944\ (7)$ Å
$b = 6·3810\ (6)$
$c = 8·1915\ (12)$
$\beta = 92·08\ (1)°$
$V = 260·89$ Å^3
Cell content: $2[Cu(IO_3)_2]$

Space group, $P2_1/m$
$D_m = 5·33\ (10)\ \mathrm{g\ cm^{-3}}$
$D_x = 5·266$
$\mu(\mathrm{Mo}\ K\alpha) = 168·6\ \mathrm{cm^{-1}}$
$\lambda(\mathrm{Mo}\ K\alpha) = 0·71069$ Å

Experimental

The X-ray intensity data were collected from a single crystal with dimensions 0·15 × 0·15 × 0·20 mm. At Uppsala 2574 independent reflections within sin θ/λ = 1·037 Å^{-1} were measured on a computer-controlled Stoe–Philips four-circle diffractometer, using Mo $K\alpha$ radiation, monochromatized by reflection from a graphite 'single' crystal. The intensity data were corrected for Lorentz, polarization and absorption effects. The absorption corrections were made using the program *DATAPH* (Lundgren, 1976); transmission factors ranged from 0·29 to 0·45. At Seattle, 1117 reflections were measured from a crystal measuring

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* Permanent address: NRC, Dokki, Cairo, Egypt.

0·12 × 0·12 × 0·20 mm on a Syntex $P\bar{1}$ diffractometer, using monochromatized Mo $K\alpha$ radiation. These data were corrected for Lorentz and polarization factors, but not for absorption.

The crystal structure was independently determined at Uppsala and Seattle through the determination of the iodine atom positions from a three-dimensional Patterson synthesis, followed by difference Fourier syntheses. The structure was refined to an R value of 0·064 at Seattle. Since these data were not corrected for absorption, we report only the results of the least-squares refinement of the structure carried out at Uppsala. For the refinement, relativistic Dirac–Slater atomic form factors for Cu^{2+}, I^0 and $O^{\frac{1}{2}-}$ (Cromer & Waber, 1965) were used, which were corrected for anomalous dispersion effects (Cromer & Liberman, 1970). The form factor for $O^{\frac{1}{2}-}$ was obtained by interpolation between those for O^0 and O^- (= $F^- - 1$). The structure was refined by minimizing $\sum w(F_o - F_c)^2$ by means of a full-matrix least-squares program *UPALS* (Lundgren, 1976). Each reflection was assigned a weight $w = 1/\sigma^2(F)$, where $\sigma^2(F) = \sigma^2_{\text{count}}(F^2)/4F^2 + K^2$. The constant K was empirically chosen as $0{\cdot}02 \times F$ for $F \geq 25{\cdot}0$ on an absolute scale, and $0{\cdot}02 \times (50{\cdot}0 - F)$ for all other reflections. 138 reflections with $F_o < 2\sigma(F_o)$ were excluded from the refinement. The total number of parameters varied was 50, which includes an overall scale factor, atomic coordinates, anisotropic thermal parameters and an isotropic extinction coefficient [final value 0·064 (8)] (Coppens & Hamilton, 1970). The very strong 040 reflection appeared to be seriously affected by extinction and not corrected appropriately; hence, it was excluded from the final refinement. The final refinement based on 2437 reflections resulted in R values, $R(F) = 0{\cdot}021$ and $R_w(F) = 0{\cdot}028$. The fit between the observed and calculated structure factors was examined by the δR normal probability plot (Abrahams & Keve, 1971).* The central portion of the plot, except for a small number of points at the extremities, is linear with a slope of 0·88 and an intercept of −0·18, indicating some deviation from a random normal distribution. The final atomic positional parameters are listed in Table 2 and the bond distances and angles in Table 3. The estimated standard deviations in bond lengths and angles (which include errors in unit-cell dimensions) are calculated from the variance–covariance matrix of the final cycle of least-squares refinement. The average standard deviations in I—O and Cu—O bond lengths are 0·002 Å and in O—I—O and O—Cu—O angles 0·01°.

Description of the structure

The crystal structure of γ-$Cu(IO_3)_2$ consists of $I(1)O_3$ and $I(2)O_3$ trigonal pyramids and distorted CuO_6 octahedra (Fig. 1).

Table 2. *Atomic positional parameters, with standard deviations in parentheses*

	x	y	z
I(1)	0·03775 (3)	0·25000	0·24151 (2)
I(2)	0·46482 (3)	0·25000	0·84414 (2)
Cu	0·50000	0·00000	0·50000
O(1)	0·25688 (33)	0·03444 (27)	0·31016 (19)
O(2)	0·80036 (41)	0·25000	0·39940 (30)
O(3)	0·25294 (37)	0·03719 (32)	0·90406 (22)
O(4)	0·36816 (42)	0·25000	0·62094 (23)

Table 3. *Interatomic distances* (Å) *and angles* (°), *with standard deviations in parentheses*

The I(1) polyhedron			
I(1)–O(1)	1·833 (2) (×2)	O(1)–I(1)–O(1′)	97·2 (1)
I(1)–O(2)	1·786 (2)	O(2)–I(1)–O(1)	100·5 (1) (×2)
Mean	1·817	Mean	99·4
I(1)–O(3)	2·600 (2) (×2)	O(1)–O(2)–O(1′)	59·2 (1)
[I(1)–O(3‴)	3·295 (2) (×2)]	O(2)–O(1)–O(1′)	60·4 (1) (×2)
		Mean	60·0
O(1)–O(1′)	2·751 (3)	O(1)–I(1)–O(3)	85·9 (1) (×2)
O(1)–O(2)	2·783 (3) (×2)	O(2)–I(1)–O(3)	87·6 (1) (×2)
O(1)–O(3)	3·074 (3) (×2)	O(3)–I(1)–O(3′)	89·6 (1)
O(2)–O(3)	3·092 (3) (×2)	O(3)–I(1)–O(1′)	170·6 (1)
The I(2) polyhedron			
I(2)–O(3)	1·801 (2) (×2)	O(3)–I(2)–O(3)	97·9 (1)
I(2)–O(4)	1·874 (2)	O(3)–I(2)–O(4)	97·6 (1) (×2)
Mean	1·825	Mean	97·7
I(2)–O(1)	2·637 (2) (×2)	O(3)–O(4)–O(3′)	58·8 (1)
I(2)–O(3)	3·064 (2) (×2)	O(4)–O(3)–O(3′)	60·6 (1) (×2)
		Mean	60·0
O(3)–O(3′)	2·716 (3)	O(3)–I(2)–O(1)	86·4 (1) (×2)
O(3)–O(4)	2·766 (3) (×2)	O(4)–I(2)–O(1)	69·8 (1) (×2)
O(3)–O(1)	3·097 (3) (×2)	O(3)–I(2)–O(3″)	68·0 (1) (×2)
O(3)–O(3″)	2·916 (3) (×2)	O(4)–I(2)–O(3″)	138·8 (1) (×2)
O(4)–O(1)	2·654 (2) (×2)	O(1)–I(2)–O(3″)	70·9 (2) (×2)
O(4)–O(3″)	4·642 (3) (×2)	O(1)–I(2)–O(3‴)	119·8 (1)
		O(1)–I(2)–O(3′)	167·2 (1)
		O(3)–I(2)–O(3‴)	121·9 (1)
		O(3″)–I(2)–O(3‴)	73·5 (1)
The Cu octahedron			
Cu–O(1)	1·950 (2) (×2)	O(1)–Cu–O(4)	95·6 (1) (×2)
Cu–O(4)	2·002 (1) (×2)	O(1)–Cu–O(4′)	84·4 (1) (×2)
Cu–O(2)	2·359 (2) (×2)	O(1)–Cu–O(2)	91·8 (1) (×2)
Mean of 4	1·976	O(1)–Cu–O(2′)	88·2 (1) (×2)
Mean of 6	2·104	O(4)–Cu–O(2)	81·9 (1) (×2)
		O(4)–Cu–O(2′)	98·1 (1) (×2)
O(1)–O(4)	2·929 (2) (×2)	Mean	90·0
O(1)–O(4′)	2·654 (2) (×2)		
O(2)–O(1)	3·107 (3) (×2)		
O(2)–O(1′)	3·014 (3) (×2)		
O(2)–O(4)	2·870 (3) (×2)		
O(2)–O(4′)	3·302 (2) (×2)		
Cation–cation (<4·0 Å) distances			
Cu–Cu	3·1905 (3)		
Cu–I(1)	3·4646 (5), 3·8281 (5)		
Cu–I(2)	3·2494 (4)		
I(1)–I(2)	3·9559 (7)		

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33519 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

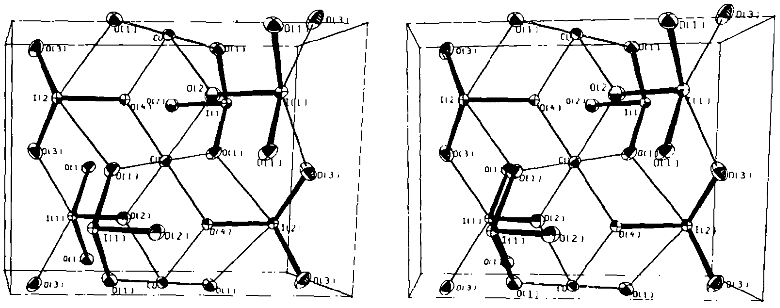


Fig. 1. Stereoscopic view of the contents of one unit cell of γ-$Cu(IO_3)_2$.

The iodate groups

I(1) has three nearest-neighbor oxygen atoms at an average distance of 1·817 Å and average O—I—O angle of 99·4°. In addition, I(1) is weakly bonded to two further oxygen atoms O(3) at 2·600 Å. The fivefold coordination around I(1) may be described as a distorted square pyramid, where O(1), O(1′), O(3) and O(3′) form a square, while O(2) serves as the apical oxygen [Fig. 2(*a*)].

I(2) has three nearest-neighbor oxygen atoms at an average distance of 1·825 Å, the average O—I—O angle being 97·7°. As in the case of I(1), iodine I(2) is also weakly bonded to two further oxygen atoms O(1), at 2·637 Å. The coordination of these five oxygens around I(2) may again be described as distorted square pyramidal with O(4) at the apex. In addition I(2) has two further oxygens, O(3), at 3·064 Å, thus increasing the coordination of I(2) to sevenfold [Fig. 2(*b*)]. Both iodate groups show the point symmetry *m*; the deviation from the highest possible point group 3*m* is indicated mostly by the weak I—O bonds.

The average short I—O distances and O—I—O angles in γ-$Cu(IO_3)_2$ (1·817 Å, 99·4° and 1·825 Å, 97·7°) compare closely with those reported for the two independent iodate ions in α-$Cu(IO_3)_2$ (1·820 Å, 97·3° and 1·819 Å, 98·8°), where the iodine atoms are coordinated by 6 and 7 oxygen atoms respectively (Liminga, Abrahams & Bernstein, 1975*b*). These dimensions also compare closely with those reported for the three independent iodate groups in $3Cu(IO_3)_2.2H_2O$, bellingerite (1·806 Å, 99·6°; 1·821 Å, 96·3° and 1·819 Å, 97·9°), where the iodine atoms are coordinated by five, six and seven oxygen atoms respectively (Ghose & Wan, 1974). The fivefold coordination of the iodine atom is relatively rare; so far it has been found only in bellingerite and γ-$Cu(IO_3)_2$. Besides α-$Cu(IO_3)_2$, γ-$Cu(IO_3)_2$, and bellingerite, sevenfold coordination of the iodine atom has been found in $Sr(IO_3)_2.H_2O$ (Manotti-Lanfredi, Pellinghelli, Tiripicchio & Camellini, 1972), $Nd(IO_3)_2.H_2O$ (Liminga, Abrahams & Bernstein, 1975*a*) and $Ca(IO_3)_2$, lautarite (Ghose, Wan & Wittke, 1978).

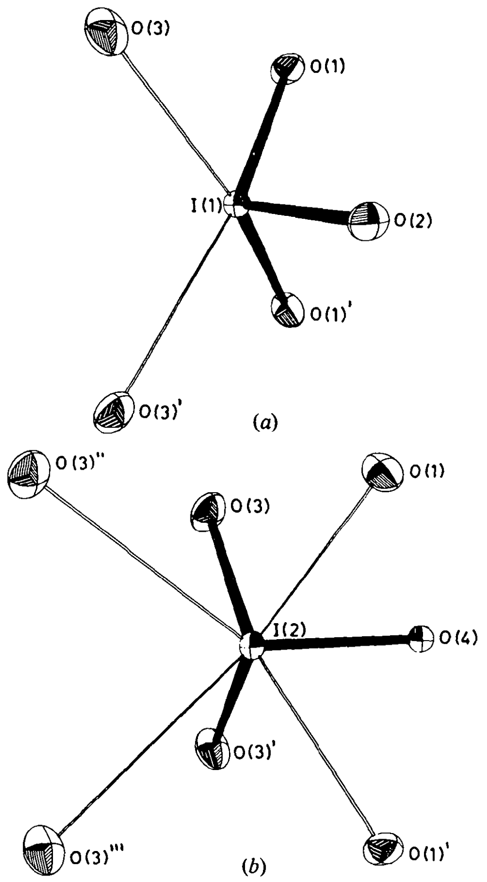
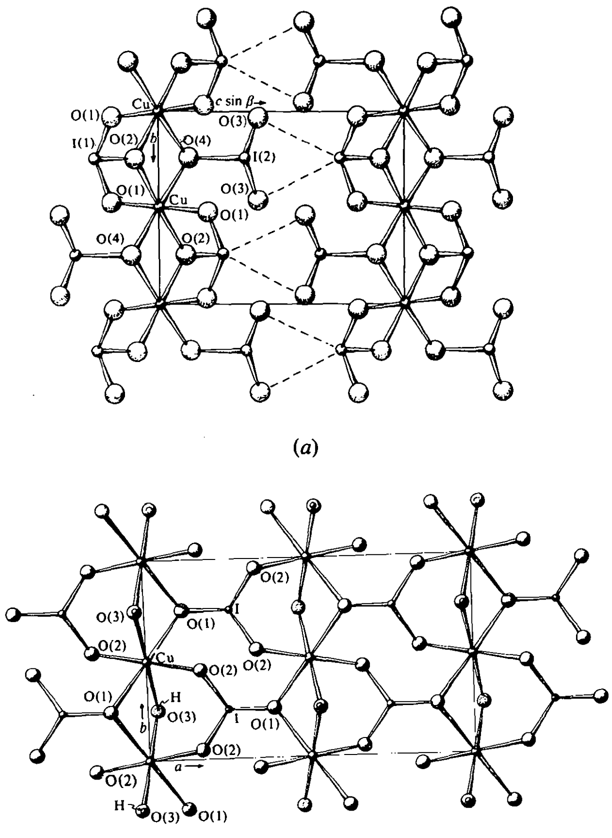


Fig. 2. (*a*) Oxygen atom configuration around I(1); (*b*) oxygen atom configuration around I(2); the short I—O bonds are shaded.

The CuO_6 *octahedron*

The CuO_6 octahedron with point symmetry $\bar{1}$, exhibits the typical Jahn–Teller type tetragonal distortion associated with the Cu^{2+} ion. The Cu—O distances within the square plane are 1·951 (×2) and 2·002 (×2) Å; two long apical Cu—O bonds, 2·359 Å, complete the octahedron. The average of the four short Cu—O



(*a*)

(*b*)

Fig. 3. (*a*) A view of the γ-Cu(IO$_3$)$_2$ structure down the *a* axis; note the Cu(IO$_3$)$_2$ columns parallel to the *b* axis. The origin of the unit cell has been shifted by $\frac{1}{2}(\mathbf{a} + \mathbf{b} + \mathbf{c})$. (*b*) A view of the CuIO$_3$(OH), salesite, structure down the *c* axis. Note the Cu(OH)IO$_3$ columns parallel to the *b* axis (after Ghose & Wan, 1978).

distances (1·976 Å) compares closely with the average of those in α-Cu(IO$_3$)$_2$ (1·973 Å); the apical bonds in α-Cu(IO$_3$)$_2$ are slightly longer (2·394 Å) than those in γ-Cu(IO$_3$)$_2$. The CuO$_6$ octahedra form a chain parallel to the *b* axis, by sharing edges with adjacent Cu octahedra (Fig. 1).

Comparison with related structures

The structure of γ-Cu(IO$_3$)$_2$ can be considered as a hexagonal close-packed array of iodate ions located at $y = \frac{1}{4}$ and $\frac{3}{4}$, forming layers parallel to the (100) plane; the Cu^{2+} ions occur in octahedral interstices between these layers at $y = 0$ and $\frac{1}{2}$. The apices of the I(1)O$_3$ and I(2)O$_3$ groups point in parallel and antiparallel directions along *a* and *c* axes respectively, accounting for the centrosymmetry.

On the other hand α-Cu(IO$_3$)$_2$ crystallizes in a polar space group, where the iodate ions form a nearly regular hexagonal close-packed array (Liminga, Abrahams & Bernstein, 1975*b*). The resulting distorted octahedral interstices are occupied by Cu^{2+} ions, displaced out of the iodine planes. This displacement gives rise to a point-charge contribution to the spontaneous polarization. An additional contribution to P_s comes from the (IO$_3$)$^-$ dipoles, as the apices of both the independent iodate ions point in the same direction along [010] (Liminga & Abrahams, 1976).

Alternatively, the structure of γ-Cu(IO$_3$)$_2$ can be considered as formed of Cu(IO$_3$)$_2$ columns parallel to the *b* axis [Fig. 3(*a*)]; these columns are held together through weak I—O bonds. In this respect, the structure of γ-Cu(IO$_3$)$_2$ is closely comparable to that of CuIO$_3$(OH), salesite (Ghose, 1962; Ghose & Wan, 1978), where similar Cu(OH)IO$_3$ columns exist parallel to the *b* axis; these columns are connected together through short I—O bonds [Fig. 3(*b*)].

The crystal structure of γ-Cu(IO$_3$)$_2$ can be derived from that of CuIO$_3$(OH) by removing half of the Cu atoms (at 0,0,0 and 0,$\frac{1}{2}$,0), and by reversing the directions of the I—O bonds in iodate groups parallel to the *b* axis, pointing along $+\mathbf{a}$ and $-\mathbf{a}$, such that the oxygen corner of the reversed I—O bond replaces the (OH) corner, shared by two Cu atoms.

The magnetic behavior of γ-Cu(IO$_3$)$_2$

γ-Cu(IO$_3$)$_2$ is antiferromagnetic, with a Néel temperature of 5 K. The paramagnetic Curie temperature is positive, indicating ferromagnetic Cu—Cu interaction (Abrahams, Sherwood, Bernstein & Nassau, 1973). In γ-Cu(IO$_3$)$_2$, each CuO$_6$ octahedron shares two opposite octahedral edges with two adjacent Cu octahedra, thereby forming infinite octahedral chains parallel to the *b* axis (Fig. 1). Two short superexchange paths are Cu—O(2)—Cu and Cu—O(4)—Cu, where the Cu—Cu separation is 3·1905 Å and Cu—O(2) and Cu—O(4) distances are 2·359 and 2·002 Å respectively. A similar octahedral chain exists in the mineral salesite, CuIO$_3$(OH) (Ghose, 1962; Ghose & Wan, 1978), which shows a possible antiferromagnetic ordering below 162 K (Abrahams, Sherwood, Bernstein & Nassau, 1973). In view of the ferromagnetic Cu—Cu interaction, a possible model for antiferromagnetic ordering in γ-Cu(IO$_3$)$_2$ calls for spins, which are collinear in each chain, but antiparallel with respect to neighboring chains.

α-Cu(IO$_3$)$_2$ is also ferromagnetic with a Néel temperature of 8·5 K. The inverse susceptibility follows the Curie–Weiss behavior at higher temperatures, corresponding to a paramagnetic moment for Cu^{2+} of 1·84 μ_B, the spin-only value for Cu^{2+} being 1·73 μ_B (Abrahams, Sherwood, Bernstein & Nassau, 1973).

The magnetic behavior is consistent with the crystal structure of α-$Cu(IO_3)_2$ (Liminga, Abrahams & Bernstein, 1975*b*), which contains isolated CuO_6 groups, the closest Cu—Cu distance (translation along the *b* axis) being 5·111 Å.

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The Crystal Structure of Antimony(III) Chloride Oxide $Sb_4O_5Cl_2$

BY CHRISTER SÄRNSTRAND

Inorganic Chemistry 2, *Chemical Center, University of Lund, PO Box* 740, *S*-220 07 *Lund* 7, *Sweden*

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The structure of $Sb_4O_5Cl_2$ has been reinvestigated and refined to an *R* of 0·031 for 1206 independent reflections. The space group is $P2_1/c$ with $a = 6{\cdot}2380$ (4), $b = 5{\cdot}1112$ (3), $c = 13{\cdot}538$ (2) Å, $\beta = 97{\cdot}217$ (8)°, $Z = 2$. The main architecture of the crystal structure is the same as found by Edstrand [*Acta Chem. Scand.* (1947). **1**, 178–203] but differences were observed, especially in the Sb—O distances. There are two crystallographically independent Sb atoms, which can both be considered three-coordinated. The coordination polyhedron can be described as a distorted tetrahedron with the lone pair of electrons (*E*) of Sb at the fourth corner. The SbO_3E polyhedra share corners forming infinite layers parallel to the *bc* plane. The Cl atoms are situated between these layers. A short survey is given of the linking of Sb—O coordination polyhedra in some Sb^{III} compounds.

Introduction

This investigation is part of a general study of the O coordination of Sb^{III}. In order to obtain accurate Sb^{III}—O distances for the discussion of the coordination geometry, it was considered necessary to refine the structure of $Sb_4O_5Cl_2$ (Edstrand, 1947).

Experimental

$Sb_4O_5Cl_2$ was prepared according to Edstrand (1947) and colourless, transparent single crystals suitable for X-ray work were obtained.

Cell dimensions were determined by a least-squares analysis of the θ values of 59 reflections (θ: 19–26°)