

The Crystal Structure of Dipotassium Hydrogen Diiodate(V) Chloride

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The crystal structure of dipotassium hydrogen diiodate(V) chloride, $K_2H(IO_3)_2Cl$, has been determined from three-dimensional X-ray intensity data (Mo $K\alpha$) measured with an automatic diffractometer. The space group is $Pca2_1$, with unit cell dimensions $a=15.100$ (18), $b=6.594$ (8), $c=8.611$ (7) Å, $V=857.4$ Å³ and $Z=4$. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares methods to an R value of 3.7% (observed reflexions only). The structure consists of IO_3^- and HIO_3 groups joined to one another by hydrogen bonds [$O(2)\cdots O(4)=2.633$ (11) Å] and by intermolecular $I\cdots O$ interactions [$I\cdots O=2.536$ (9) Å], to form zigzag chains parallel to a . Bridging chloride ions link the chains in layers, parallel to (001). The average planes of these layers lie at $z=\frac{1}{4}$ and $z=\frac{3}{4}$; in between, the potassium cations at $z\approx 0$ and $z\approx \frac{1}{2}$, together with intermolecular oxygen-iodine interactions $I\cdots O=2.932$ (9) and 2.946 (9) Å, connect the layers. The bond distances in the two independent IO_3 groups are: $I(1)-O=1.846$ (8), 1.809 (9), 1.767 (9) Å and $I(2)-O=1.801$ (9), 1.773 (9), 1.927 (8) Å. The last distance, much longer than the others, is probably an $I-OH$ distance. The environment of each iodine atom is completed by two oxygen atoms of different pyramidal anions and by a chloride anion; the resulting coordination polyhedron can be described as a distorted octahedron.

Introduction

In connexion with our work on salts of oxyacids of iodine(V) and iodine(VII), the crystal structures of calcium diiodate(V) hexahydrate (Braibanti, Manotti Lanfredi, Pellinghelli & Tiripicchio, 1971) and of strontium diiodate(V) monohydrate (Manotti Lanfredi, Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1972) have been determined in this laboratory. The purpose of these investigations is to determine the structure of the iodate group, IO_3 , and to elucidate the conditions determining the high coordination numbers of the pentavalent iodine atoms in the crystals. In fact the iodine atom of the iodate group is surrounded, apart from the covalently bound oxygen atoms, by other atoms, mainly by oxygen atoms of adjacent anions, by water molecules, or by halide ions. The coordination by chloride ions has been found in a preliminary investigation of dipotassium hydrogen diiodate(V) chloride (Braibanti, Tiripicchio & Manotti Lanfredi, 1967). For this compound the poor quality of the intensity data, photographically recorded by rotation around one axis, prevented an accurate determination of the structural details. Consequently a new set of diffractometric intensity data has now been collected by counter methods and the results of the complete structure determination are reported here.

Experimental

Preparation

The crystals were prepared in the form of stable, colourless prisms by slow evaporation of a solution of potassium iodate in dilute hydrochloric acid.

Crystal data

Dipotassium hydrogen diiodate(V) chloride, $K_2H(IO_3)_2Cl$

Formula weight: 464.5

Crystal class: rhombic pyramidal

Unit-cell parameters (determined from rotation and Weissenberg photographs and refined on an automated single-crystal diffractometer, Mo $K\alpha$ radiation, $\lambda=0.71069$ Å):

$a=15.100$ (18), $b=6.594$ (8), $c=8.611$ (7) Å,

$V=857.4$ Å³, $Z=4$,

$D_x=3.60$, $D_m=3.64$ g.cm⁻³,

$\mu(\text{Mo } K\alpha)=86.65$ cm⁻¹, $F(000)=840$.

Space group: $Pca2_1$ (C_{2v}^5 , No. 29) from systematic absences and structure determination. The crystals are piezoelectric.

Intensity data

The intensities were collected on a single crystal automated Siemens diffractometer on line with a Siemens 304/P computer using Zr-filtered Mo $K\alpha$ radiation and the $\omega-2\theta$ scan technique. A thin prismatic crystal of approximate dimensions $0.043 \times 0.070 \times 0.170$ mm was aligned with its [001] axis along the ϕ axis of the diffractometer and all the reflexions with $2\theta \leq 72^\circ$ were collected. 2134 independent reflexions were measured and 1329 were used in the crystal analysis, taking as unobserved those reflexions whose intensities were less than twice their standard deviations $\{\sigma^2(I)=[\text{total counts}+(0.005I)^2]\}$.

Calculations

After the usual Lorentz and polarization corrections, the intensities were put on absolute scale by Wilson's

Table 1. Fractional atomic coordinates with e.s.d.'s ($\times 10^4$)

	x	y	z
I(1)	2177 (1)	0648 (1)	2500
I(2)	5343 (1)	4926 (1)	2406 (1)
K(1)	4840 (2)	0190 (4)	4815 (3)
K(2)	7346 (2)	4379 (4)	-0096 (3)
Cl	6239 (2)	2239 (4)	7088 (3)
O(1)	1152 (5)	1868 (14)	3203 (11)
O(2)	2862 (5)	2882 (13)	2288 (18)
O(3)	1944 (6)	0207 (17)	0517 (10)
O(4)	4591 (5)	2646 (12)	1937 (13)
O(5)	6264 (5)	3331 (14)	2929 (11)
O(6)	5547 (6)	5528 (16)	0431 (10)

(1942) method. No correction for absorption was made.

The positions of the iodine atoms were located from a three-dimensional Patterson function. The positions of the other non-hydrogen atoms were determined by successive Fourier syntheses. The refinement was carried out by means of cycles of full-matrix least-squares; at the beginning isotropic, and in the later cycles anisotropic thermal parameters were introduced. Unit weights were used at first, then the scheme: $1/w = (A + BF_o)^2$, was assumed; the coefficients $A = 2.4$ and $B = 0.0142$ were determined by plotting ΔF against F_o . At the end of the refinement, R was 3.7%.

Table 2. Anisotropic thermal parameters with e.s.d.'s (\AA^2)

The B_{ij} values refer to the formula: $\exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$ in which $b_{11} = \frac{1}{2}a^2B_{11}$, $b_{12} = \frac{1}{2}a^*b^*B_{12}$, etc.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I(1)	0.572 (12)	0.992 (18)	0.882 (14)	0.081 (12)	0.016 (22)	0.144 (25)
I(2)	0.637 (13)	1.028 (20)	0.881 (14)	0.113 (10)	0.106 (21)	-0.075 (28)
K(1)	1.237 (96)	1.948 (105)	1.744 (74)	0.228 (71)	0.092 (73)	-0.106 (77)
K(2)	1.161 (103)	2.276 (98)	1.718 (78)	0.232 (55)	0.185 (75)	-0.061 (86)
Cl	0.803 (60)	1.704 (79)	1.896 (90)	0.230 (57)	-0.133 (61)	0.064 (69)
O(1)	0.704 (243)	2.230 (362)	2.467 (337)	0.616 (217)	0.483 (223)	0.543 (272)
O(2)	0.911 (187)	1.606 (243)	2.820 (582)	-0.404 (187)	-0.025 (319)	0.102 (316)
O(3)	1.465 (292)	3.935 (501)	0.923 (258)	0.236 (273)	-0.464 (210)	-0.909 (284)
O(4)	1.549 (257)	0.670 (234)	4.069 (568)	-0.212 (210)	0.167 (279)	-0.844 (260)
O(5)	0.936 (220)	2.041 (318)	2.315 (335)	0.836 (220)	-0.287 (221)	0.063 (247)
O(6)	1.441 (289)	2.908 (390)	1.095 (249)	0.427 (257)	-0.009 (213)	0.219 (261)

Table 3. Environment of the iodine atoms

Pyramidal anions			
I(1)-O(1)	1.846 (8) \AA	O(1)-O(2)	2.781 (12) \AA
I(1)-O(2)	1.809 (9)	O(1)-O(3)	2.825 (13)
I(1)-O(3)	1.767 (9)	O(2)-O(3)	2.713 (15)
I(2)-O(4)	1.927 (8)	O(4)-O(5)	2.705 (12)
I(2)-O(5)	1.801 (9)	O(4)-O(6)	2.716 (13)
I(2)-O(6)	1.773 (9)	O(5)-O(6)	2.810 (13)
O(1)-I(1)-O(2)	99.1 (4) $^\circ$	O(2)-O(1)-O(3)	57.9 (4) $^\circ$
O(1)-I(1)-O(3)	102.8 (4)	O(1)-O(2)-O(3)	61.9 (3)
O(2)-I(1)-O(3)	98.6 (6)	O(1)-O(3)-O(2)	60.3 (4)
O(4)-I(2)-O(5)	93.0 (4)	O(5)-O(4)-O(6)	62.5 (3)
O(4)-I(2)-O(6)	94.4 (5)	O(4)-O(5)-O(6)	59.0 (3)
O(5)-I(2)-O(6)	103.7 (4)	O(4)-O(6)-O(5)	58.6 (3)
Interanion contacts			
I(1)-O(3 ⁱⁱ)	2.932 (9) \AA	I(2)-O(6 ^{iv})	2.946 (9) \AA
I(1)-O(5 ⁱⁱ)	2.987 (9)	I(2)-O(1 ^v)	2.536 (9)
I(1)-Cl ⁱⁱⁱ	3.078 (4)	I(2)-Cl ^{vi}	3.046 (4)
O(1)-I(1)-O(5 ⁱⁱ)	87.4 (3) $^\circ$	O(5)-I(2)-O(1 ^v)	92.7 (3) $^\circ$
O(5 ⁱⁱ)-I(1)-Cl ⁱⁱⁱ	80.2 (2)	O(1 ^v)-I(2)-Cl ^{vi}	83.7 (2)
O(2)-I(1)-Cl ⁱⁱⁱ	92.7 (3)	O(4)-I(2)-Cl ^{vi}	89.9 (2)
O(3)-I(1)-O(5 ⁱⁱ)	83.3 (4)	O(6)-I(2)-O(1 ^v)	89.4 (4)
O(3)-I(1)-Cl ⁱⁱⁱ	86.7 (3)	O(6)-I(2)-Cl ^{vi}	85.0 (3)
O(3 ⁱ)-I(1)-O(2)	84.9 (5)	O(6 ^{iv})-I(2)-O(4)	80.6 (4)
O(3 ⁱ)-I(1)-O(1)	97.6 (3)	O(6 ^{iv})-I(2)-O(5)	94.1 (3)
O(3 ⁱ)-I(1)-O(5 ⁱⁱ)	90.7 (3)	O(6 ^{iv})-I(2)-O(1 ^v)	93.7 (3)
O(3 ⁱ)-I(1)-Cl ⁱⁱⁱ	71.9 (2)	O(6 ^{iv})-I(2)-Cl ^{vi}	77.5 (2)
O(3 ⁱ)-I(1)-O(3)	158.4 (4)	O(6 ^{iv})-I(2)-O(6)	161.8 (4)
O(1)-I(1)-Cl ⁱⁱⁱ	163.5 (3)	O(4)-I(2)-O(1 ^v)	172.3 (3)
O(2)-I(1)-O(5 ⁱⁱ)	172.6 (3)	O(5)-I(2)-Cl ^{vi}	170.6 (3)

Asymmetric units

i	$\frac{1}{2} - x, y, \frac{1}{2} + z$	vii	$\frac{1}{2} + x, \bar{y}, z$
ii	$x - \frac{1}{2}, \bar{y}, z$	viii	$1 - x, \bar{y}, \frac{1}{2} + z$
iii	$1 - x, \bar{y}, -\frac{1}{2} + z$	ix	$x, y, z - 1$
iv	$1 - x, 1 - y, \frac{1}{2} + z$	x	$\frac{3}{2} - x, y, z - \frac{1}{2}$
v	$\frac{1}{2} + x, 1 - y, z$	xi	$x, y, 1 + z$
vi	$1 - x, 1 - y, -\frac{1}{2} + z$	xii	$\frac{3}{2} - x, y, \frac{1}{2} + z$

The final atomic coordinates are quoted in Table 1 and the thermal parameters in Table 2. A table of observed and calculated structure factors is available as Supplementary Publication No. SUP 30004 (11 pp.).*

The atomic scattering factors of Cromer & Mann (1968) were used: those for I, Cl and K were corrected for the real and imaginary part of the anomalous dispersion using the values for $\Delta f'$ and $\Delta f''$ given in *International Tables for X-ray Crystallography* (1965).

All calculations were performed on the CDC 6600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Bologna), using the programs written by Immirzi (1967).

Description of the structure

The structure consists of IO_3 groups, both as anions IO_3^- and molecules HIO_3 , and of chloride and potassium ions. The IO_3^- anions, corresponding to I(1), and the acid molecules HIO_3 , corresponding to I(2), are joined alternately to form zigzag chains parallel to a (Fig. 1). The linkages between each I(1) O_3 and the two HI(2) O_3 adjacent in the chain are a strong hydrogen bond $\text{O}(2)\cdots\text{O}(4)=2.633$ (11) Å and a dipole-ion interaction $\text{I}(2)\cdots\text{O}(1)=2.536$ (9) Å. The assignment of the hydrogen atom to O(4), although not located in the difference map, has been done on the basis of the long bond $\text{I}(2)-\text{O}(4)=1.927$ (8) Å (Table 3), which in-

dicates a single-bond character as expected for an I-OH bond.

Sets of zigzag chains are held together by bridging Cl^- anions in layers parallel to (001) and by weak $\text{I}\cdots\text{O}$ interactions of 2.987 (9) Å. Each Cl^- anion is bound by an ion-dipole interaction directly to the iodine atoms I(1) [$\text{Cl}\cdots\text{I}(1)=3.078$ (4) Å] and I(2) [$\text{Cl}\cdots\text{I}(2)=3.046$ (4) Å]. The average planes of these layers lie approximately at $z=\frac{1}{4}$ and $z=\frac{3}{4}$ (Fig. 2); the connections between the layers are determined by weak interactions $\text{I}\cdots\text{O}=2.932$ (9) and 2.946 (9) Å, and by ionic bonds with the cations K(1) and K(2), which lie approximately in the intermediate planes at $z=0$ and $z=\frac{1}{2}$.

Both iodate groups are pyramidal with distances $\text{I}-\text{O}=1.846$ (8), 1.809 (9), 1.767 (9) Å for I(1) and $\text{I}-\text{O}=1.801$ (9), 1.773 (9) and $\text{I}-\text{OH}=1.927$ (8) Å for I(2). The sum of the angles $\text{O}-\text{I}(1)-\text{O}$ is 300.5° and that of the angles $\text{O}-\text{I}(2)-\text{O}$ is 291.1° , indicating a small flattening of the former. The I-O distances are comparable with those found in other compounds, which have been tabulated in a previous paper (Braibanti, Manotti Lanfredi, Pellinghelli & Tiripicchio, 1971) and

Table 4. *Environments of the potassium ions*

K(1)-Cl	3.181 (5) Å	K(2)-Cl ^x	3.177 (5) Å
K(1)-Cl ⁱⁱⁱ	3.276 (4)	K(2)-Cl ^{ix}	3.266 (4)
K(1)-O(3 ⁱ)	2.761 (10)	K(2)-O(5 ^x)	2.788 (9)
K(1)-O(1 ^{vii})	2.774 (9)	K(2)-O(2 ^v)	2.843 (13)
K(1)-O(4)	2.984 (11)	K(2)-O(6)	2.856 (10)
K(1)-O(4 ^{viii})	2.752 (10)	K(2)-O(2 ^v)	2.904 (14)
K(1)-O(6 ^{iv})	2.932 (11)	K(2)-O(3 ^{vii})	3.129 (12)
		K(2)-O(5)	3.152 (10)

* This table has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30004. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

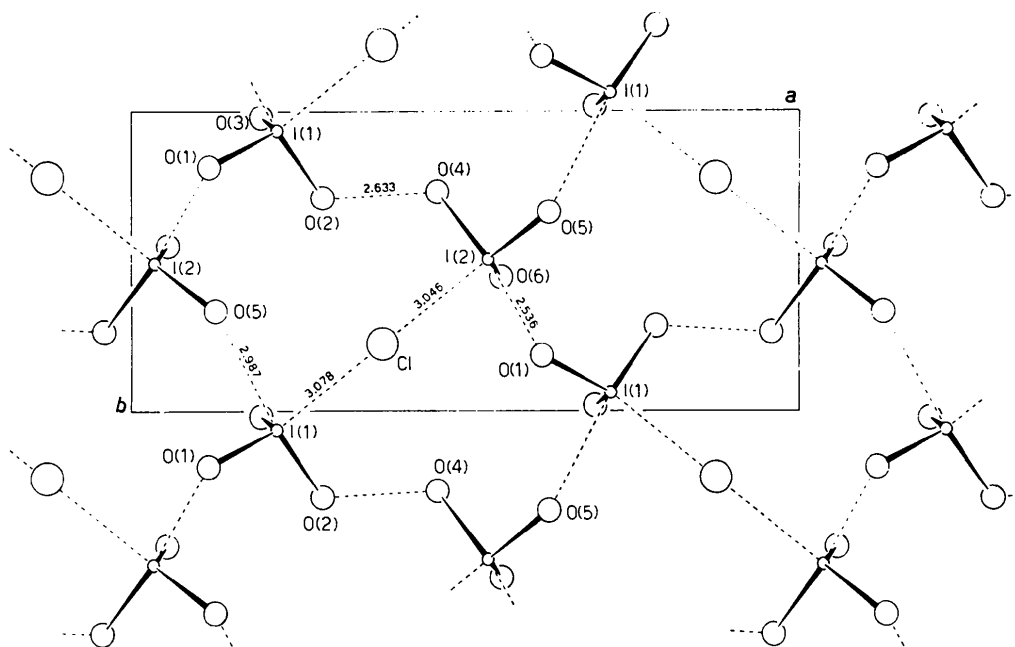


Fig. 1. Projection of a layer of the structure on the plane (001).

also with the values found by Chan & Einstein (1971) in $\text{KIO}_3 \cdot \text{HIO}_3$.

The environment of the two iodine atoms is completed by interactions with chloride ions and oxygen atoms of different anions. The resulting coordination polyhedron around each iodine atom is approximately octahedral (Fig. 3): three corners of the octahedron are occupied by the oxygens of the pyramidal group itself, two corners by oxygens of IO_3^- or HIO_3 groups and the remaining corner by a chloride ion, shared between I(1) and I(2). All these contacts are shorter than the sum of the van der Waals radii and longer than single bonds. Similar types of coordination have been found in other iodates (Braibanti, Manotti Lanfredi, Pellinghelli & Tiripicchio, 1971). A possible clue to the explanation of these additional bonds can be found in other compounds of pentavalent iodine and in the iso-electronic compounds of hexavalent xenon. In the structure of xenon trioxide, XeO_3 (Templeton, Zalkin,

Forrester & Williamson, 1963), the xenon atom of the pyramidal group XeO_3 is surrounded by three oxygen atoms of other pyramids at distances of $\sim 2.8 \text{ \AA}$. The analogy is particularly significant because XeO_3 and IO_3^- are isoelectronic. Other parallel examples can be found in the structures of $\text{XeF}_2 \cdot \text{IF}_5$ (Jones, Burbank & Bartlett, 1970) and in that of XeF_6 (Burbank & Jones, 1970). In the former the square pyramidal IF_5 is bound through an $\text{I} \cdots \text{F}$ interaction to XeF_2 and in the latter the cation XeF_3^+ is bound through a $\text{Xe} \cdots \text{F}^-$ interaction to the fluoride anion. The electrostatic attraction between the surrounding oxygen or chlorine atoms and the positive central atom, whose positive charge is only partially shielded by the electron lone pair, determines the formation of dipole-dipole and ion-dipole bonds. Further arguments in favour of the electrostatic interpretation of these bonds in the iodates are the various coordination numbers and the irregular geometry of the coordination polyhedra and the varia-

Table 5. *Environment of the chloride ion*

Cl-I(2 ^{iv})	3.046 (4) Å	Cl-K(1)	3.181 (5) Å
Cl-I(1 ^{viii})	3.078 (4)	Cl-K(2 ^{xi})	3.266 (4)
Cl-K(2 ^{xii})	3.177 (5)	Cl-K(1 ^{viii})	3.276 (4)
K(1)—Cl-K(1 ^{viii})	84.4 (1)°	I(1 ^{viii})—Cl-K(1)	108.9 (1)°
K(1 ^{viii})—Cl-K(2 ^{xi})	86.2 (1)	I(1 ^{viii})—Cl-K(1 ^{viii})	90.1 (1)
K(2 ^{xi})—Cl-K(2 ^{xii})	84.5 (1)	I(1 ^{viii})—Cl-K(2 ^{xi})	77.5 (1)
K(2 ^{xii})—Cl-K(1)	105.7 (1)	I(1 ^{viii})—Cl-K(2 ^{xii})	79.6 (1)
I(2 ^{iv})—Cl-K(1)	78.2 (1)	I(1 ^{viii})—Cl-I(2 ^{iv})	168.2 (1)
I(2 ^{iv})—Cl-K(1 ^{viii})	81.1 (1)	K(1)—Cl-K(2 ^{xi})	168.6 (1)
I(2 ^{iv})—Cl-K(2 ^{xi})	94.0 (1)	K(1 ^{viii})—Cl-K(2 ^{xii})	167.4 (1)
I(2 ^{iv})—Cl-K(2 ^{xii})	107.9 (1)		

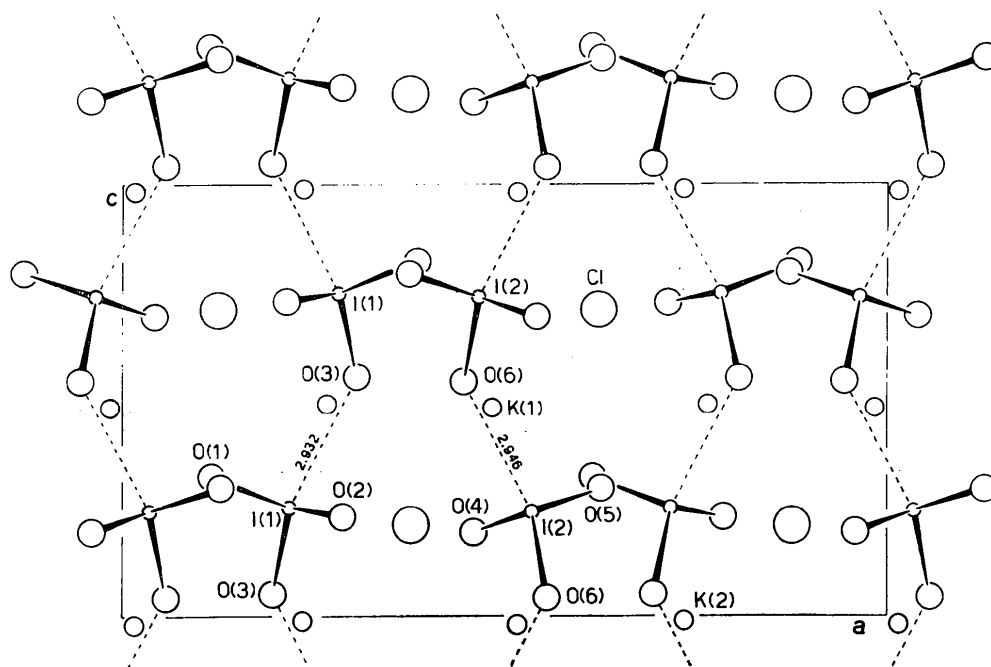


Fig. 2. Projection of the whole structure on the plane (010).

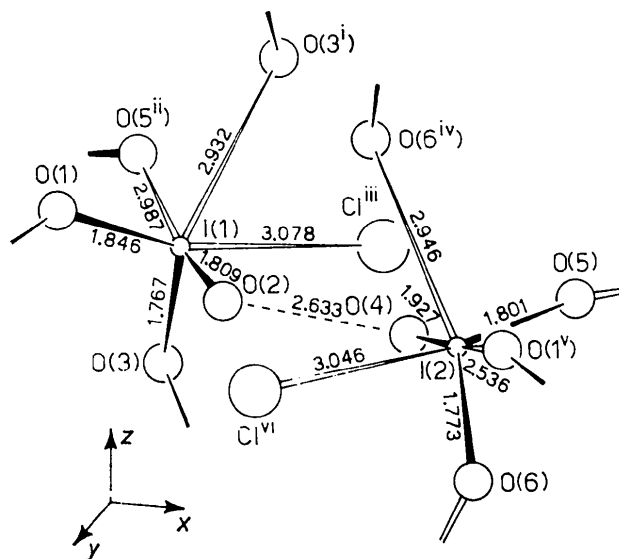


Fig. 3. Environment of the iodine atoms.

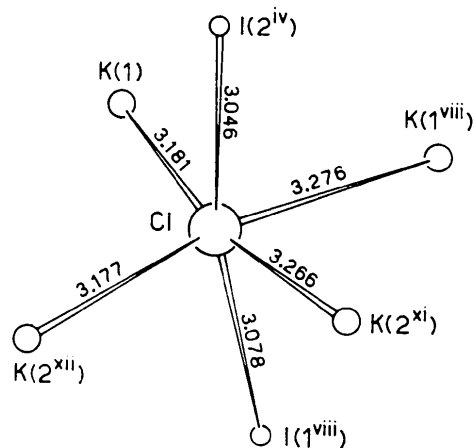


Fig. 5. Environment of the chloride ion.

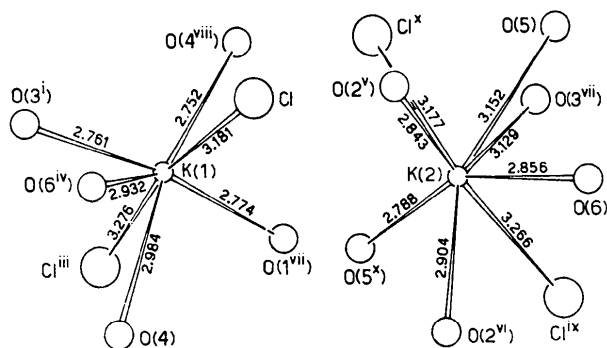


Fig. 4. Environments of the two independent potassium ions.

tion of the $I \cdots O$ distances, ranging from 2.5 to 3.2 Å. Particularly short $I \cdots O$ interactions, of length ~ 2.5 Å, occur in the present compound and in $KIO_3 \cdot HIO_3$ (Chan & Einstein, 1971) only with the iodine atom of the HIO_3 group and not when the iodine is part of the anion IO_3^- , probably because the electron distribution in the anions is such as to lower the dipole moment.

The two independent potassium ions are surrounded by oxygen and chlorine atoms, but the coordination cannot be described in terms of a distorted polyhedron

(Fig. 4). Distances shorter than 3.30 Å are reported in Table 4.

The environment of the chloride ions is approximately octahedral (Fig. 5), with the two iodine atoms at opposite corners. The bond lengths and angles in the octahedron are given in Table 5.

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References

- BRAIBANTI, A., MANOTTI LANFREDI, A. M., PELLINGHELLI, M. A. & TIRIPICCHIO, A. (1971). *Inorg. Chim. Acta*, **5**, 590. the press.
- BRAIBANTI, A., TIRIPICCHIO, A. & MANOTTI LANFREDI, A. M. (1967). *Chem. Commun.* p. 1128.
- BURBANK, R. D. & JONES, G. R. (1970). *Science*, **168**, 248.
- CHAN, L. Y. Y. & EINSTEIN, F. W. B. (1971). *Canad. J. Chem.* **49**, 468.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321.
- IMMIRZI, A. (1967). *Ric. Sci.* **37**, 743.
- International Tables for X-ray Crystallography* (1965). Vol. III. Birmingham: Kynoch Press.
- JONES, G. R., BURBANK, R. D. & BARTLETT, N. (1970). *Inorg. Chem.* **9**, 2264.
- MANOTTI LANFREDI, A. M., PELLINGHELLI, M. A., TIRIPICCHIO, A. & TIRIPICCHIO CAMELLINI, M. (1972). *Acta Cryst.* **B28**, 679.
- TEMPLETON, D. H., ZALKIN, A., FORRESTER, J. D. & WILLIAMSON, S. M. (1963). *J. Amer. Chem. Soc.* **85**, 817.
- WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.