The Structural Chemistry of Binary Halogen Oxides in the Solid State

Martin Jansen* **and Thorsten Kraft**

Institut für Anorganische Chemie der Universität Bonn,
Gerhard-Domagk-Straße 1, D-53121 Bonn, Germany

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The development of new preparative and analytical techniques that allow appropriate handling and characterizations of the capricious halogen oxides have initiated a revival of their chemistry. Due to these recent activities, the amount of well-confirmed knowledge about such oxides has considerably increased. This is especially valid for the structural chemistry in the solid state, which (among other topics) has greatly benefitted from developments in the techniques of in situ crystal growth of low melting substances on a diffractometer. As a consequence, some general crystal chemical features have become apparent: The coordination polyhedra of the halogen oxides can be readily understood in terms of the qualitative VSEPR concept, and there is a pronounced tendency to form mixed valence compounds where the respective valence states can be easily deduced from the coordination polyhedra. Furthermore, intermolecular or interionic bonds are significant, with increasing importance when moving from chlorine to iodine. Finally, ClO_2 appears to be the only representative with the halogen in an even oxidation state.

Introduction

Halogen oxides have been known for at least 180 years. Their compositions, syntheses and properties belong to the basic knowledge about inorganic substances that is taught in almost all kinds of introductory courses in inorganic chemistry. But, even for the binary halogen oxides, their chemistry is only rudimentarily known, and many claims that have been included into textbooks have actually not yet been properly confirmed. This unsatisfactory situation is a consequence of the notorious instability of halogen oxides, especially those containing chlorine and bromine. Thus, handling these substances during preparative or analytical work is highly difficult and even hazardous. Except for I_2O_5, all binary halogen oxides are thermodynamically unstable, and in addition most of them are of low kinetic stability.

Since the late seventies research on halogen oxides has been intensified, mainly because of their crucial role in the depletion of stratospheric ozone. Within this context interest has been focused on small molecules in the gaseous state, on their photochemistry, the kinetics of their formation and decomposition, and their spectroscopic properties. The results of these efforts have been collected in the Air Pollution Research Report no. 55 of the European Commission[1].

Another impetus that has led to an increase in activity in the field of halogen oxides has been the availability of advanced techniques for determining crystal structures of substances with low melting points. Overall, the application of improved preparative and analytical methods has produced many new reliable insights that make the former review[2] on halogen oxides at least in parts obsolete.

Martin Jansen, born in 1944 on Pellworm, Germany, studied chemistry in Giessen, where he received his PhD in 1973 under the supervision of R. Hoppe. After his habilitation in 1978 he accepted a professorial chair of Inorganic Chemistry in Hannover before he moved to Bonn in 1987. His main research interests lie in the fields of preparative solid-state chemistry, crystal chemistry, material research, and the structure-property relationship of solids. He has been awarded, among others, the Gottfried Wilhelm Leibniz prize, the Otto Bayer prize and the Alfred Stock prize.

Thorsten Kraft was born in 1964 in Brunsbüttelkoog, Germany, and studied chemistry in Bonn. In 1991, he joined the group of M. Jansen and received his PhD in 1995. Until the end of 1996 he continued his research on the solid-state and crystal chemistry of iodine-oxygen compounds.

MICROREVIEWS: This feature introduces Berichte's readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

In Table 1, all known binary halogen oxides have been listed and classified with respect to the degree and reliability of their characterizations. Oxides that have been mentioned in the literature without reliable evidence for their existence have not been included.

In this review we will focus on crystal structure determinations of solid halogen oxides. In addition to the crystal structures of the binary compounds (ClO_2[17], Cl_2O_6[26], Cl_2O_7[29], Br_2O_3[37], I_2O_4[44], I_2O_5[48], and I_2O_6[51]) also HI_3O_8[52,53], and $Br_2O_5 \cdot 3\,C_2H_5CN$[39] as well as $(IO)_2SO_4$[54], $I_3O_6HSO_4$[55], and $(IO_2)_2S_2O_7$[56] will be considered. HI_3O_8 and $Br_2O_5 \cdot 3\,C_2H_5CN$ may be viewed as molecules of I_2O_5 or Br_2O_5 embedded in matrices of HIO_3 or C_2H_5CN, respectively. The polycations $(IO)_n^{n+}$ and $(I_3O_6)_n^{n+}$ and the dication $(IO_2)_2^{2+}$, which are present in the sulfates, show marked structural relations to binary iodine oxides.

Table 1. Survey of existing binary halogen oxides

Compound	Existence	Pure comp. preparation	Constitution	Molecular structure	Crystal structure
Cl–O–Cl	[3]	+[4]	+[5]	+[5]	–
Cl–Cl–O	[6]	–	+[7]	–	–
Cl–O	[8]	–	+[9]	+[9]	–
Cl–O–Cl–O	[10]	–	+[10]	–	–
Cl–O–O–Cl	[11]	–	+[11]	+[11]	–
Cl–ClO_2	[12]	–	+[12]	+[12]	–
Cl_2O_3	[13]	–	–	–	–
O–Cl–O	[14]	+[15]	+[16]	+[16]	+[17]
Cl–O–O	[18]	–	+[18]	–	–
Cl–O–ClO_3	[19]	+[19]	+[20]	+[21]	–
ClO_3	[22]	–	+[22]	+[22]	–
Cl_2O_6	[23]	+[24]	+[25]	–	+[26]
Cl_2O_7	[27]	+[28]	+[29]	–	+[29]
ClO_4	[30]	–	+[30]	+[30]	–
Br–O–Br	[31]	+[32]	+[33]	+[33]	–
Br–Br–O	[34]	–	+[34]	–	–
Br–O	[35]	–	+[36]	+[36]	–
Br_2O_2	[34]	–	–	–	–
Br_2O_3	[37]	+[37]	+[37]	–	+[37]
O–Br–O	[38]	–	+[38]	–	–
Br–O–O	[38]	–	+[38]	–	–
Br_2O_5	[39]	–	+[39]	+[39]	+[39]
		–			
I–O	[40]	–	+[41]	+[41]	–
I_2O_4	[42]	+[43]	+[44]	–	+[44]
I_4O_9	[45]	+[46]	–	–	–
I_2O_5	[47]	+[47]	+[48]	–	+[48]
I_2O_6	[49–50]	+[50,51]	+[51]	–	+[51]

Structure Descriptions

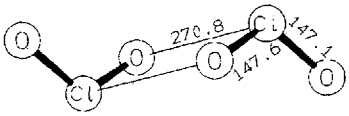
Chlorine Oxides

To date, the existence of 14 different chlorine oxides has been confirmed. Five of them are available as pure substances in macroscopic amounts, three of which have been characterized by crystal structure determination; the remaining ones have been characterized only by means of vibrational and UV-Vis spectroscopy. We will discuss the crystal structures in detail.

ClO_2: ClO_2, the first halogen oxide ever obtained, is the only one possessing an odd number of electrons that is also available as a pure substance in the condensed state. It belongs to the rather extended family of bent triatomic entities like O_3^- or NF_2, which have 19 valence electrons and show remarkable thermodynamic and kinetic stability and varying tendency to dimerize. Previously it has been claimed that ClO_2 would not dimerize in the solid state[57]: Based on IR and Raman data it has been deduced that it would crystallize isotypically to SO_2. Thus, in analogy to the crystal structure of SO_2[58], the electric dipoles should show a ferroelectric order, and the baricenters of the molecules should be arranged in cubic close packing.

Recently, single crystal growth of ClO_2 has been achieved by a modified Stockbarger-Brideman technique in capillaries in situ on a four-cycle X-ray diffractometer[17]. At first glance, the crystal structure of ClO_2 (Figure 1) consists of isolated molecules, and the bond lengths and angles resemble closely those of gaseous ClO_2[16]. However, the bond angle is a little smaller, and the lengths of the bonds between the chlorine atom and the two crystallographically independent oxygen atoms differ slightly but significantly from each other.

Figure 1. Dimer of ClO_2 molecules in the crystal[a]



[a] Molecular parameters at −150°C, intramolecular angle O–Cl–O = 115.6°.

In contrast to the crystal structure of SO_2, the electric dipoles in the crystal structure of ClO_2 show an antiferroelectric ordering, whereas the molecular arrangement shows no relation to any kind of close packing. The most pronounced difference between the crystal structures of ClO_2 and SO_2 is found in the shortest intermolecular contacts. In SO_2, they correspond approximately to the sum of the van der Waals radii. In ClO_2, however, there is one intermolecular Cl−O contact of 271 pm that is significantly shorter than the others, which represent typical van der Waals interactions in the range 300−320 pm. The shortening of this intermolecular Cl−O distance is very similar to that occurring in solid NO for side-on dimerization[59]. This effect has been attributed to a "head-to-tail" association of two molecules of ClO_2 (Figure 1) caused by an overlap of the *p* orbitals perpendicular to the plane of the ClO_2 monomers. This dimerization should result in a spin compensation, which has in fact been observed[17]. The transformation from paramagnetic to diamagnetic behavior occurs at −93 °C. Temperature-dependent crystal structure determinations in the range from −75 to −150 °C[17b] did not reveal any structural phase changes, although the intermolecular bond length is shortened by 7.0 pm whereas both intramolecular bond lengths are increased by 0.7 pm.

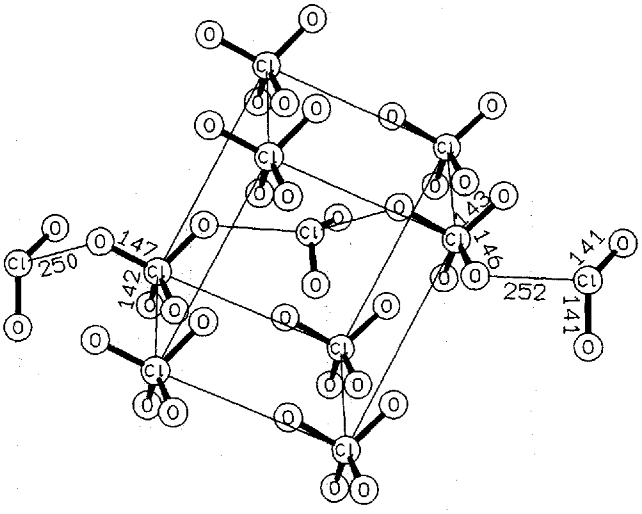
In the MO picture the intermolecular bonding situation can be described by an overlap of the *p* orbitals, producing two MO's of symmetries a_u (bonding) and a_g (antibonding) with respect to the dimer (symmetry C_i). When filling the MO's with two electrons, the lowest lying states are ^1A_g (bonding) and ^3A_u (nonbonding). As the long intermolecular bond indicates, the energy difference between them should only be small. The population of the ^3A_u state decreases with decreasing temperature, resulting in diamagnetic behavior. By this intermolecular interaction, the electron in the antibonding MO b_1 of the monomer is concentrated in one Cl−O bond, which explains the above-mentioned elongation of this Cl−O bond relative to the other.

Based on theoretical valence-bond studies[60] it has been suggested that the existence of the extremely long intermolecular bonds is due to the inability of the theoretical bond order to exceed a value of 0.125. This is the result of spin pairing of the single electrons in the $(ClO_2)_2$ dimer, whereas the single electrons occupy the $2b_1$ MO's in the case of the monomer. Furthermore, nonbonding repulsions between lone pairs of electrons are important.

Cl_2O_6: Cl_2O_6 is best prepared by reaction of ClO_2 with O_3 in a stream of O_2[24]. The yield has been considerably improved by mixing the starting gases at 0 °C using a Daniell tap and filling the reaction vessel with Raschig rings[26]. Purification by fractional condensation yields a crystalline red solid (m.p. 3 °C), which can be stored below −30 °C without decomposition. Single crystals suitable for crystal structure determination have been obtained by sublimation from −2 °C to −25 °C. The data collection was carried out at −70 °C[26].

Surprisingly, it has been found that the crystal structure of Cl_2O_6[26] is composed of isolated ClO_2^+[61,62] and ClO_4^- ions (Figure 2). The arrangement of the complex ions resembles that observed in the CsCl type. The ClO_2^+ dipoles are ordered ferroelectrically. While the structural parameters for the ClO_2^+ ions in Cl_2O_6 are in good agreement with C_{2v} symmetry, the ClO_4^- ions are significantly distorted. The two oxygen atoms with the longest Cl(VII)−O bond lengths exhibit additional weak contacts of approximately 250 pm to the Cl(V) atoms of the chloryl ions (Figure 2). In this way, the coordination of the Cl(V) atom is increased from ψ-triangular to distorted ψ-trigonal bipyramidal. This type of interionic interaction leads to one-dimensional infinite chains.

Figure 2. Crystal structure of Cl_2O_6 emphasizing the CsCl arrangement of complex ions; interionic contacts indicated by weak lines[a]



[a] Intraionic bond angles O−Cl−O at −70 °C: 109−111° in ClO_4^-; 119° in ClO_2^+.

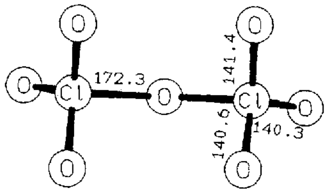
The constitution of Cl_2O_6 in the solid state is different from its molecular structure in the gas and liquid phases. According to IR studies of the gaseous state[25], Cl_2O_6 forms $O_2Cl{-}O{-}ClO_3$ molecules with C_s symmetry that have to be regarded as the mixed anhydride of chloric and perchloric acids. This molecular structure seems to be preformed in the ionic crystal structure by the interionic interactions mentioned. Similarily, a molecular structure has also been proposed for the liquid state[63].

Cl_2O_7: Single crystals of Cl_2O_7 have been grown at the melting point of −92 °C in situ on a four-circle X-ray diffractometer. Data collection was carried out at −160 °C[29].

As expected for the anhydride of perchloric acid, the crystal structure of dichlorine heptaoxide[29] contains isolated $O_3Cl{-}O{-}ClO_3$ molecules (Figure 3). Compared to the terminal Cl−O bonds, the intermolecular bridging Cl−O bonds are remarkably long. Thus, a polar description $(ClO_3^{\delta+})_2O^{2\delta-}$ has been proposed as an alternative. The Cl_2O_7 molecules exhibit C_2 symmetry, the deviations from C_{2v} being very small. A view along the Cl−Cl direction in the molecule reveals a staggered conformation of the terminal oxygen atoms. No intermolecular distances below the sum of the van der Waals radii of Cl and O are detected.

The extended solid-state structure may be described by assuming a distorted face-centered cubic packing of the oxygen atoms with the chlorine atoms located in neighboring pairs of tetrahedral holes[29].

Figure 3. Molecular structure of Cl_2O_7 in the solid state[a]



[a] Intramolecular bond angles at −160 °C: O_t–Cl–O_t = 114.8 and 115.8°; O_t–Cl–O_b = 105.0, 105.2 and 97.7°; Cl–O–Cl = 116.6°.

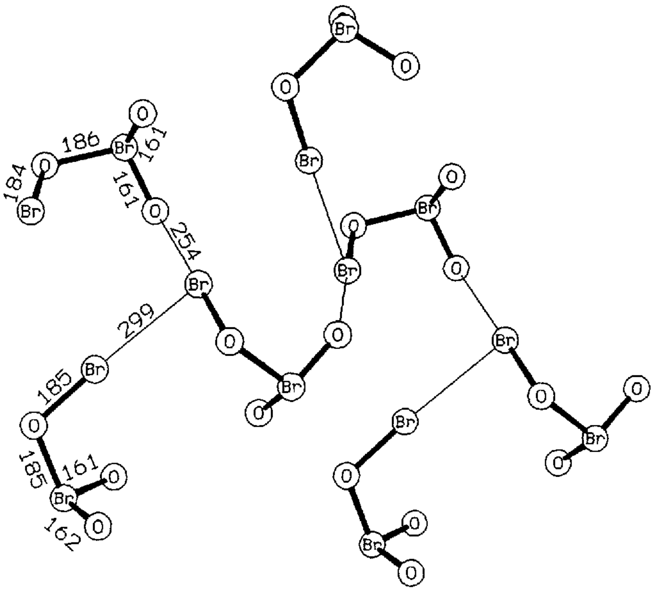
Bromine Oxides

Two bromine oxides can be prepared as pure compounds, and a further one cocrystallizes with propionitrile. Five others have been trapped and characterized in cryogenic noble gas matrices or investigated in the gas phase. So far, two crystal structures have been determined. The molecular parameters of Br_2O_3[37] and Br_2O_5[39] (obtained from single crystal data) as well as of Br_2O[33] (derived from EXAFS-data) are summarized in Table 2. The existence of bromine perbromate, Br–O–BrO_3[64], is very doubtful. Most probably the samples investigated were mixtures of Br_2O_3 and Br_2O_5[37,39]. Below, we discuss the crystal structures of Br_2O_3 and $Br_2O_5 \cdot 3\ C_2H_5CN$ in detail.

Br_2O_3: Slow ozonization of a solution of bromine in $CFCl_3$ at approximately −55 °C yields a lemon-yellow solid. Extraction of the solid with a small amount of CH_2Cl_2 at −78 °C yields an orange solution from which Br_2O_3 precipitates as orange needles upon cooling to −90 °C. The crystals decompose above −40 °C[37].

According to the results of the crystal structure determination[37], dibromine trioxide is not the anhydride of bromous acid, $HBrO_2$. Instead, it should be considered bromine bromate, Br(I)–O–Br(V)O_2, the mixed anhydride of hypobromic and bromic acid. This is in agreement with the general instability of Br(III)–oxygen compounds. To date, bromites and even dilute aqueous solutions of bromous acid are unknown, whereas hypobromites, bromates, and aqueous solutions of hypobromous and bromic acid are well known. The crystal structure (Figure 4) contains two distinct crystallographically independent Br(I)–O–Br(V)O_2 molecules, which are bent at the intramolecular bridging oxygen atom and exhibit *syn* conformation. The Br(V) atoms show ψ-tetrahedral coordination. Deviation from ideal C_s symmetry is negligibly small for one crystallographically independent Br(I)–O–Br(V)O_2 molecule but severe for the other.

Figure 4. Crystal structure of Br_2O_3[a]



[a] Intramolecular bond angles: O_t–Br(V)–O_t = 106 and 109°, O_t–Br(V)–O_b = 103–104°, Br(III)–O–Br(V) = 111 and 112°.

Additional intermolecular interactions have to be considered (Figure 4). Weak contacts between the terminal bromine atom and one of the terminal oxygen atoms connect one of the two crystallographically independent molecules (with C_s symmetry) with two neighbor molecules, resulting in the formation of infinite zigzag chains. In contrast, the remaining molecules are isolated from each other on opposite sides of the chain. Only very weak Br(I)···Br(I) interactions are encountered with the Br(I) atoms of the undistorted molecules.

$Br_2O_5 \cdot 3\ C_2H_5CN$: Ozonization of a solution of bromine in CH_2Cl_2 at −78 °C yields a yellow or colorless precipitate that decomposes above −40 °C. The powder can be recrystallized from propionitrile at temperatures between −50 and −90 °C, yielding large colorless needles with the composition $Br_2O_5 \cdot 3\ C_2H_5CN$ that decompose above −20 °C[39].

The crystal structure determination of the compound that cocrystallizes with bromine pentoxide and propionitrile[39] reveals Br_2O_5 molecules (Figure 5). Their constitution, O_2Br–O–BrO_2, agrees with that expected for the anhydride of bromic acid. Each Br(V) atom is coordinated

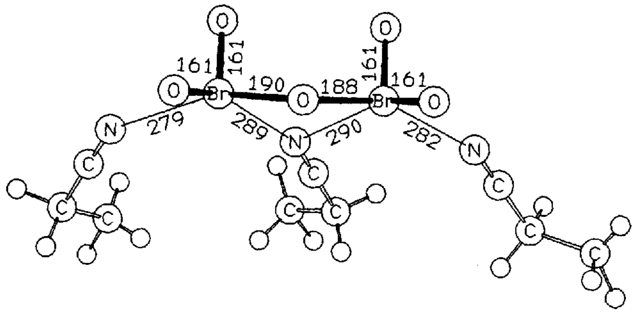
Table 2. Selected average bond lengths (in pm) and bond angles (in °) for bromine oxides[a]

	d(Br(III)–O_t)	d(Br(III)–O_b)	d(Br(I)–O_b)	$\sphericalangle$(Br–O_b–Br)	$\sphericalangle$(O_b–Br–O_t)	$\sphericalangle$(O_t–Br–O_t)
Br–O–Br[b]	–	–	185	112	–	–
Br–O–BrO_2[c][37]	161.2	185.5	184.5	111.7	103.1	107.6
O_2Br–O–BrO_2[c][39]	160.9	188.6	–	121.2	94.6/103.0	109.5

[a] O_t = Terminal oxygen atom, O_b = intramolecular bridging oxygen atom. – [b] By EXAFS data[33]. – [c] By single-crystal X-ray work.

to three oxygen atoms and one lone pair, resulting in considerably distorted ψ-tetrahedra. With respect to the Br–Br axis of the molecule, the conformation is *syn*-periplanar and the point-group symmetry is approximately C_s.

Figure 5. Crystal structure of $Br_2O_5 \cdot 3\ C_2H_5CN$[a]



[a] Bond angles: O_t–Br–O_t = 109–110°, O_t–Br–O_b = 94–95 and 103°, Br–O–Br = 121°.

To a first approximation, the Br_2O_5 and C_2H_5CN molecules are isolated in the crystal structure. However, the shortest contacts N···Br indicate interactions that complete the coordination sphere of the Br(V) atoms (Figure 5). Thus, the coordination of the bromine atoms can be described as severely distorted ψ-octahedral. The intermolecular Br···N contacts appear to play a role in the stabilization of bromine pentaoxide, as indicated by the increase in the decomposition temperature from −40 °C for pure Br_2O_5 to −20 °C for $Br_2O_5 \cdot 3\ C_2H_5CN$.

Iodine Oxides

Four of the five confirmed binary iodine oxides can be prepared as pure bulk materials and three of them have been characterized by crystal structure determination. The crystal structures of iodosyl sulfate[54], $I_3O_6HSO_4$[55], anhydro iodic acid[52,53], and diiodyl disulfate[56] are included in the descriptions below, because they show remarkable relations to the structures of the binary iodine oxides, and thus allow further insight into the structure chemistry of iodine oxygen compounds.

I_2O_4: Microcrystalline samples of diiodine tetraoxide form during hydrolysis of iodosyl sulfate on a porous plate in air, probably according to the reaction[65]:

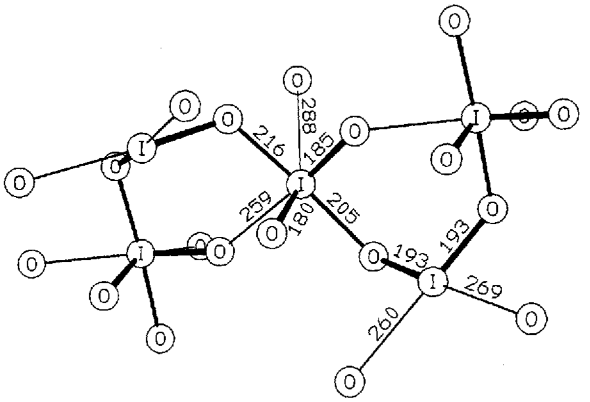
$$4\ (IO)_2SO_4 + 4\ H_2O \rightleftharpoons 3\ I_2O_4 + I_2 + 4\ H_2SO_4.$$

Most of the H_2SO_4 evolved is drained by the porous plate, but I_2 and the residual H_2SO_4 are removed by carefully washing the product with absolute ethanol. Since it has not been possible to grow single crystals suitable for crystal structure analysis, the crystal structure has been solved by means of X-ray and neutron-powder techniques[66,44].

Iodine dioxide is a mixed valent I(III)/I(V) oxide. Since various I–O distances up to 300 pm have to be considered, the structure is discussed in order of increasing interatomic distances. Considering all bond lengths up to 200 pm, the structure seems to be simply ionic, best described as iodyl iodite ($IO_2^+IO_2^-$), with bent iodyl ions {*d*[I(V)–O]: 180 and 185 pm, O–I–O: 97°} and iodite ions {*d*[I(III)–O]: 2 × 193 pm, O–I–O: 95.8°}. Short interionic contacts up to 216 pm between the oxygen atoms of the IO_2^- ions and the I(V) atom of the IO_2^+ ions are clearly bonding in character, thus forming polymeric $[I(V)O_2{-}O{-}I(III){-}O]_n$ zigzag chains (Figure 6a). Within the range of distances considered so far, the I(V) atoms are coordinated ψ-trigonal bipyramidally by four oxygen atoms and one lone pair.

The intrachain I(V)–O···I(V) contacts of 259 pm seem to be responsible for the helical tertiary structure of the zigzag chain. The interionic I(III)···O bonds of 260 and 269 pm may be considered as still weakly bonding, and would therefore connect the chains to a two-dimensional infinite layer.

Figure 6. Polymeric $(IO_2^+IO_2^-)_n$ chain in the crystal structure of diiodine tetraoxide with additional I···O contacts[a]



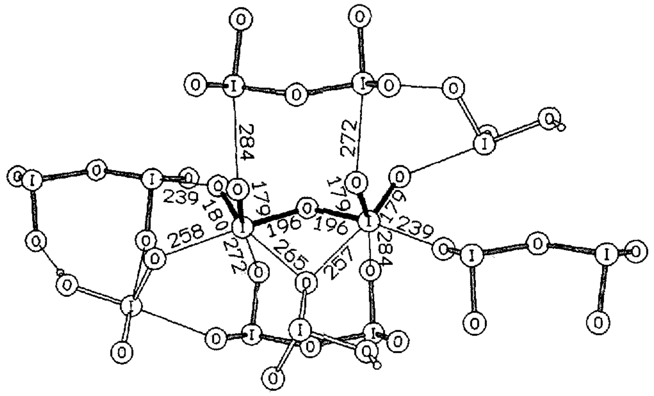
[a] Intrachain bond angles: O_b–I(III)–O_b = 96°, O_t–I(V)–O_t = 97°, O_t–I(V)–O_b = 87–93°, O_b–I(V)–O_b = 176°, I(V)–O–I(III) = 120–121°.

I_2O_5 and HI_3O_8: Both iodine pentoxide (I_2O_5)[48] and anhydroiodic acid (HI_3O_8)[52,53], which represents a cocrystallizate of I_2O_5 and HIO_3, contain molecular $O_2I{-}O{-}IO_2$ units, as would be expected for the anhydride of iodic acid. The I(V) atoms are coordinated ψ-tetrahedrally by three oxygen atoms and one lone pair. The conformation of the molecular units is *syn*-clinal in iodine pentoxide, and *syn*-periplanar in anhydroiodic acid.

Additional intermolecular I···O contacts have to be considered in both cases. In anhydroiodic acid, each iodine atom of the I_2O_5 unit is coordinated to three additional terminal oxygen atoms from neighboring I_2O_5 or HIO_3 molecules, forming distorted $I(V)O_6$ octahedra (Figure 7a). The intermolecular interactions exceeding the van der Waals interactions in iodine pentaoxide cover a rather wide range. The stronger ones have to be discussed in some detail (Figure 7b): The shortest I···O contacts, of 223 pm, connect the I_2O_5 units "head to head", forming broad one-dimensional infinite ribbons. If one now includes the I···O contacts of 245 and 254 pm, a three-dimensional infinite network results.

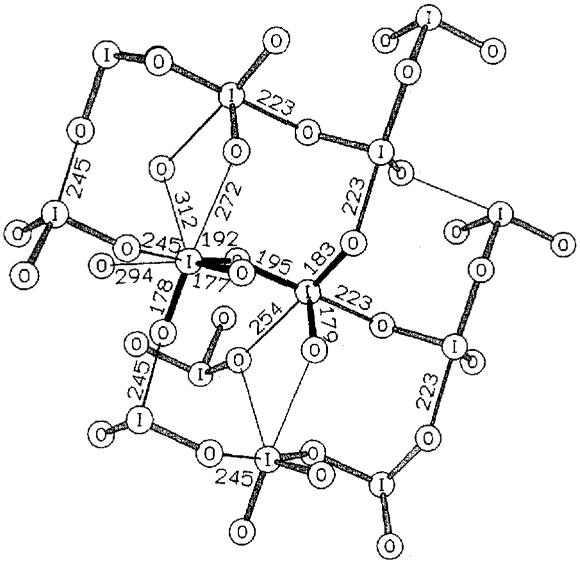
I_2O_6: Diiodine hexaoxide[49,50] is best prepared by the slow decomposition of a solution of H_5IO_6 in conc. H_2SO_4 at 70 °C, resulting in both pure and coarse crystalline yellow

Figure 7a. Coordination of an I_2O_5 molecule in the crystal structure of anhydrous iodic acid[a]



[a] Intramolecular bond angles: O_t-I-O_t = 96 and 98°, O_t-I-O_b = 88–97°, $I-O-I$ = 126°.

Figure 7b. Crystal structure of iodine pentoxide[a]

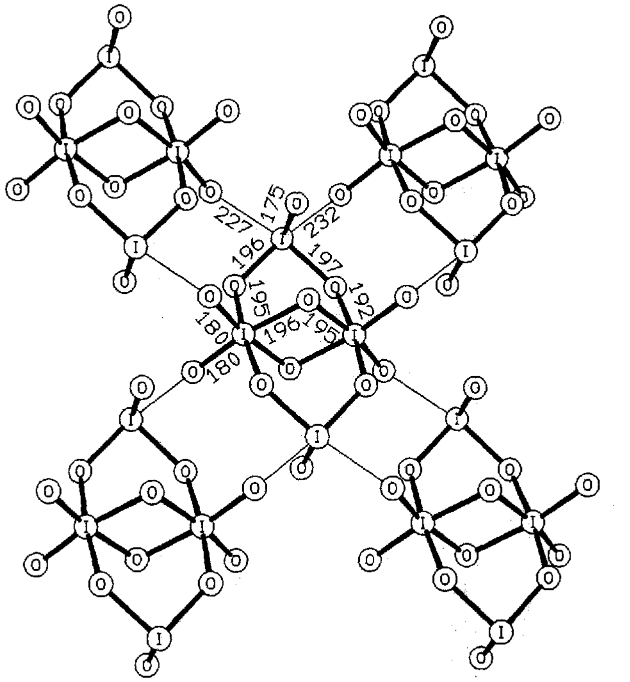


[a] Intramolecular bond angles: O_t-I-O_t = 95 and 100°, O_t-I-O_b = 93–102°, $I-O-I$ = 139°.

crusts. Under these conditions, lanceolate single crystals are formed.

The crystal structure of the mixed-valent I(V)/I(VII) oxide contains molecular I_4O_{12} units that can be regarded as being formed by two I(VII) octahedra connected via a common edge and two pyramidal IO_3 units that share two of their vertices with the axial positions of this "double octahedron" (Figure 8). Thus, the I_4O_{12} unit can be regarded as the mixed anhydride of two molecules each of H_5IO_6 and HIO_3. Within experimental error, the point symmetry of the I_4O_{12} unit is C_{2h}. The I_4O_{12} units are connected via strong I(VII)–O···I(V) intermolecular contacts up to 232 pm to two-dimensionally infinite layers (Figure 8). These intermolecular bonds are 35% shorter than the van der Waals contact distance of iodine and oxygen, and increase the coordination of the I(V) atoms towards a distorted tetragonal pyramid.

Figure 8. Layer of I_4O_{12} molecules in the crystals structure of diiodine hexaoxide[a]



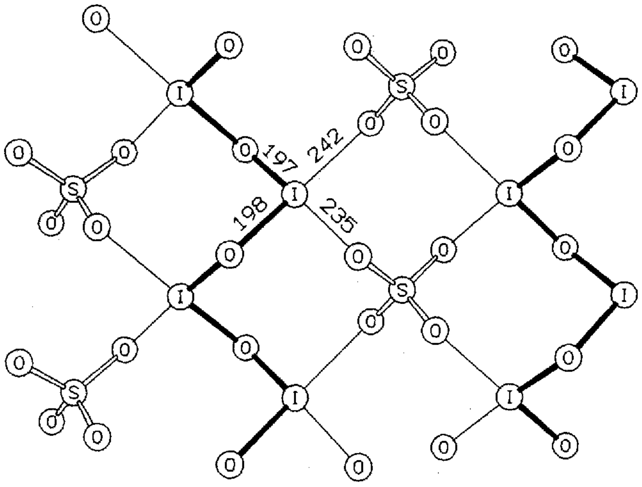
[a] Bond angles: $O_t-I(VII)-O_t$ = 102°, $O_t-I(VII)-O_bI(VII)$ = 89–91 and 167–169°, $O_t-I(VII)-O_bI(V)$ = 90–91 and 93–94°, $I(VII)O_b-I(VII)-O_bI(VII)$ = 78°, $I(VII)O_b-I(VII)-O_bI(V)$ = 87–88°, $I(V)O_b-I(VII)-O_bI(V)$ = 174°, $O_t-I(V)-O_b$ = 99 and 101°, $O_b-I(V)-O_b$ = 92°, $O_t-I(V)\cdots O$ = 88–89°, $O_b-I(V)\cdots O$ = 81–82 and 169–171°, $O\cdots I(V)\cdots O$ = 104°, $I(VIII)-O-I(VII)$ = 102°, $I(VII)-O-I(V)$ = 129°, $I(VII)-O\cdots I(V)$ = 129–132°.

$(IO)_2SO_4$: Iodosyl sulfate [$(IO)_2SO_4$ or $I_2O_3 \cdot SO_3$] is synthesized from I_2O_5 and I_2 in conc. H_2SO_4[65]. Single crystals were grown by recrystallization from a hot solution in conc. H_2SO_4.

To a first approximation, the crystal structure of $(IO)_2SO_4$ consists of isolated sulfate ions with nearly T_d symmetry and polymeric $(I-O^+)_n$ spiral chains (Figure 9). The two intrachain I–O bond lengths are equal, within the limit of experimental error. Relatively short interionic contacts between the I(III) atoms and the oxygen atoms of the sulfate groups connect the ions, forming a layer structure. In this way, the I(III) atoms are coordinated by four oxygen atoms in an almost planar arrangement. Viewed in this way, the two lone pairs would be located opposite to each other, perpendicular to the plane of the oxygen atoms.

$I_3O_6HSO_4$: For the synthesis of $I_3O_6HSO_4$, HIO_3 or H_5IO_6 is dissolved and subsequently decomposed in anhydrous phosphoric acid by heating to 310–330°C until the evolution of iodine starts. After cooling in vacuo in a desiccator for several hours, conc. H_2SO_4 is added. After a few days, the resulting precipitate of $I_3O_6HSO_4$ is filtered off and dried on a porous plate or by washing with F_3CCOOH. Single crystals were grown by using anhydrous H_2SO_4 instead of conc. H_2SO_4, and afterwards keeping the resulting clear solution in ampoules at 60°C for 8 days. Under these conditions $I_3O_6HSO_4$ forms bright yellow, very hygroscopic crystals[55].

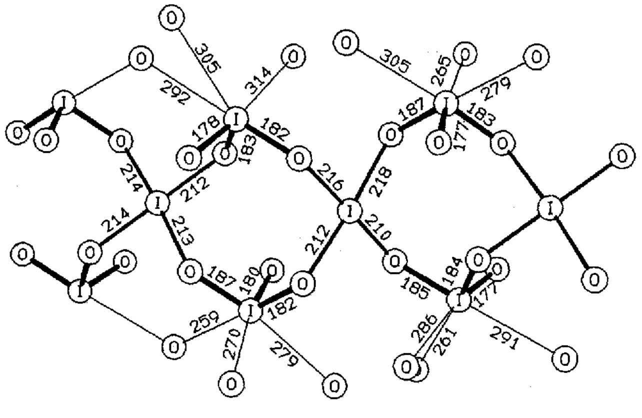
Figure 9. Layer in the crystal structure of iodosyl sulfate[a]



[a] Bond angles: O–I–O = 95°, O–I···O = 84–88 and 175–176°, O···I···O = 94°.

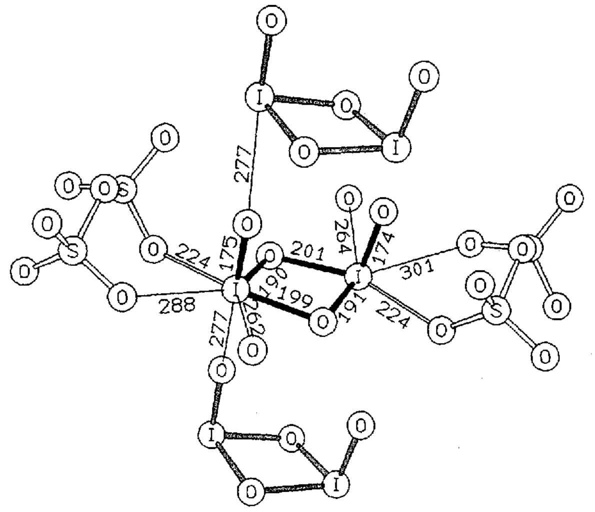
$I_3O_6HSO_4$ contains the I(III)/I(V) mixed-valence polymeric cation $(I_3O_6^+)_n$ (Figure 10). The wavelike isopolycation is shaped like a ribbon and includes two trigonal pyramidal $I(V)O_3$ groups per I(III) atom. Each I(III) atom exhibits a slightly distorted square planar coordination to four oxygen atoms, thus forming a ψ^2-octahedron with two lone pairs. The $I(III)O_4$ groups are connected via all four corners and two of the $I(V)O_3$ oxygen atoms to I(V), leading to the one-dimensional infinite ribbon. The structural groups in this network, which are identified as typical for I(III) and I(V) respectively, could mislead one to formulate the cationic part of the structure as $[I^{3+}(IO_3^-)_2]^+$ or $[(IO^{3+})_2IO_4^{5-}]^+$. Although this would indeed furnish a perfectly clear interpretation of the constitution of the cation, it would not properly account for the dominant covalent bonding. The HSO_4^- anions are connected via H-bridges, resulting in infinite chains. The cationic and anionic structural moieties are arranged parallel to each other. The coordination of each I(V) atom is completed by the addition of three oxygen atoms at a distance of 259–314 pm, which belong either to other $(I_3O_6^+)_n$ chains or to HSO_4^- ions.

Figure 10. The $(I_3O_6^+)_n$ polycation in the crystal structure of $I_3O_6HSO_4$[a]



[a] Bond angles: $O_b{-}I(III){-}O_b$ = 84–97 and 175–179°, $O_t{-}I(V){-}O_b$ = 95–105°, $O_b{-}I(V){-}O_b$ = 94–98°, I(III)–O–I(V) = 123–128°.

Figure 11. Crystal structure of diiodyl disulfate[a]



[a] Bond angles: $O_t{-}I{-}O_b$ = 97–99°, $O_b{-}I{-}O_b$ = 77°, $O_t{-}I{\cdots}O$ = 91–93°, $O_b{-}I{\cdots}O$ = 78–80 and 154–156°, I–O–I = 102°.

$(IO_2)_2S_2O_7$: A product of composition $I_2O_5 \cdot 2\ SO_3$ is obtained by heating I_2O_5 with an excess of liquid SO_3 to 100 °C in a closed glass tube for 24 h[67]; alternatively it can be prepared by dissolving iodic acid in 20% oleum at 195 °C. Pure, colorless coarse crystalline samples are obtained by slowly cooling the mixture to room temperature[56].

The crystal structure shows that diiodyl disulfate consists of dimeric iodyl dications and disulfate groups (Figure 11). Two bent IO_2^+ groups are connected through two common oxygen atoms, forming asymmetric bridges between the two iodine atoms. The resulting four-membered ring is nearly planar. The two terminal oxygen atoms in the dication are placed at one side, approximately perpendicular to this plane. On dimerization the coordination of each iodine atom becomes trigonal pyramidal. Short interionic S–O···I contacts of 224 pm connect the complex ions into a one-dimensional infinite chain with an alternating sequence of the $(IO_2)_2$ and S_2O_7 groups. Considering also the mentioned S–O···I bond, the I(V) atoms are now coordinated ψ-trigonal bipyramidally.

Concluding Remarks

Though the sytematics of halogen oxides still seems to be incomplete, the main structural characteristics are already becoming clear. Using an extreme simplification, all structures may be reduced to small charged or uncharged molecular units that can be well understood in terms of conventional qualitative models for covalent bonding. In each case the coordination spheres found are in agreement with the VSEPR concept. Closed electronic shells are observed, except for ClO_2. Other candidates that had been suspected to be radicals, e.g. Cl_2O_6 and I_2O_6, have proved to be mixed

Table 3. Variations of I−O bond lengths and correlation to their crystal chemical function in iodine oxides

Compound	Strong intramolecular contacts, 173−202 pm formulation/coordination		Medium intermolecular contacts, 209−246 pm formulation/coordination		Weak intermolecular contacts, 254−315 pm formulation/coordination	
I_2O_4[44]	$IO_2^+IO_2^-$	ψ-trig. pl. $I(V)O_2^+$ ψ^2-tetrah. $I(III)O_2^-$	${}^{1}_{\infty}(I_2O_4)_n$	ψ-trig. bipy. $I(V)O_4$ ψ^2-tetrah. $I(III)O_2^-$	${}^{3}_{\infty}(I_2O_4)_n$	irreg. $I(V)O_6$ planar $I(III)O_4$
I_2O_5[48]	I_2O_5	ψ-tetrah. $I(V)O_3$	${}^{2}_{\infty}(I_2O_5)_n$	ψ-trig. bipy. $I(V)O_4$	${}^{3}_{\infty}(I_2O_5)_n$	irreg. $I(V)O_5$, $I(V)O_7$
HI_3O_8[53]	I_2O_5	ψ-tetrah. $I(V)O_3$	${}^{1}_{\infty}(I_2O_5)_n$	ψ-trig. bipy. $I(V)O_4$	${}^{3}_{\infty}(HI_3O_8)_n$	octah. $I(V)O_6$
I_2O_6[51]	I_4O_{12}	octah. $I(VII)O_6$ ψ-tetrah. $I(V)O_3$	${}^{2}_{\infty}(I_4O_{12})_n$	octah. $I(VII)O_6$ ψ-octah. $I(V)O$	no weak contacts	
$(IO)_2SO_4$[54]	${}^{1}_{\infty}(IO)_n$	ψ^2-tetrah. $I(III)O_2$	${}^{2}_{\infty}(I_2SO_6)_n$	ψ^2-octah. $I(III)O_4$	no weak contacts	
$I_3O_6HSO_4$[55]	$[I^{3+}(IO_3^+)_2]^+$	ψ-tetrah. $I(V)O_3^+$ isolated I^{3+}	${}^{2}_{\infty}(I_3O_6^+)_n$	ψ-tetrah. $I(V)O_3$ ψ^2-octah. $I(III)O_4$	${}^{3}_{\infty}(HI_3SO_{10})_n$	irreg. $I(V)O_6$ ψ^2-octah. $I(III)O_4$
$(IO_2)_2S_2O_7$[56]	$(IO_2^+)_2$	ψ-tetrah. $I(V)O_3$	${}^{1}_{\infty}(I_2S_2O_{11})_n$	ψ-trig. bipy. $I(V)O_4$	${}^{3}_{\infty}(I_2S_2O_{11})_n$	irreg. $I(V)O_6$, $I(V)O_7$

valent. Viewing the halogen oxides in this simplified way is tempting, because it facilitates both classification and comprehension. In the solid state, however, this description does not take the real chemical bonding within these systems appropriately into account. With the exception only of Cl_2O_7 there exist strong or at least clearly significant intermolecular interactions. With respect to their strength, these intermolecular bonds range from regular covalent single bonds to van der Waals type interactions. Thus, as a characteristic feature, halogen oxides form oligomeric or polymeric structures in the solid state. Although the variation in intermolecular distances seems to be almost continuous, discrimination into three classes appears possible: (1) regular covalent intramolecular bonds (bond order >0.9); (2) strong intermolecular interactions (bond order ca. 0.3−0.9); (3) weak intermolecular interactions (bond order ca. 0.1 to ca. 0.3). Such a classification is shown in Table 3 for the iodine compounds. Since these bonds of intermediate strength are typical for halogen oxides and have not yet been understood quantitatively (c.f. the ClO_2 dimer), this phenomenon clearly deserves the attention of theoreticians. For the experimentalists there also remains much to be done, e.g. the synthesis of Cl_2O_5, Br_2O_7 and I_2O_7, which from the point of view of systematics should exist.

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