Synthesis and Crystal Structure of Diiodine(V/VII) Hexaoxide: An Intermediate between a Molecular and a Polymer Solid

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Received March 17, 1995

Exploring the field of binary halogen oxides has always been a task of particular intricacy. Except for I_2O_5, which is well established,[1] all oxides of the halogens are thermodynamically unstable. Therefore, it is not surprising that, in spite of almost 200 years of investigation, our knowledge about this important class of inorganic compounds remained rather fragmentary. Recently, significant progress has been achieved in understanding the chemistry of the oxides of chlorine and bromine.[2] In contrast, the situation for the oxides of iodine has barely improved, so far.

In the literature[3] or even in textbooks numerous oxides of iodine are mentioned which in general are not properly confirmed. In many instances the compositions given are questionable because of preparative problems, and the proposed structures are speculative because of the lack of reliable and unambiguous experimental spectroscopic or X-ray data. Iodine oxides are usually prepared from complex mixtures, are polymeric in structure, and are thermally labile. Many experimental parameters have to be controlled precisely, and the formation of well-defined solid phases is often ruled by solubility differences. Thus, reproducible syntheses of iodine oxides as crystalline, pure samples are a real challenge.

During our efforts toward the preparation and characterization of binary oxides with iodine in an oxidation state higher than +V, a procedure for the synthesis of pure bulk iodine trioxide was developed. Its preparation by thermal decomposition of H_5IO_6[4] or by dehydration of an equimolar solution of H_5IO_6 and HIO_3 in 95% H_2SO_4 by oleum[5] has been described previously in the literature. However, all samples obtained via these routes were contaminated with side products or H_2SO_4. Furthermore, a previously proposed structure, consisting of $(IO_2^+)_n$ chains and IO_4^- groups,[5] was suspect.

Our improved method for the synthesis of iodine trioxide yields for the first time pure, coarse crystalline samples in gram amounts.[6] Single-crystal X-ray analysis[7] reveals the structure illustrated in Figure 1. In contrast to the earlier proposal,[5] the structure consists of molecular subunits of composition I_4O_{12} (Figure 2) which are linked through iodine–oxygen bridges.

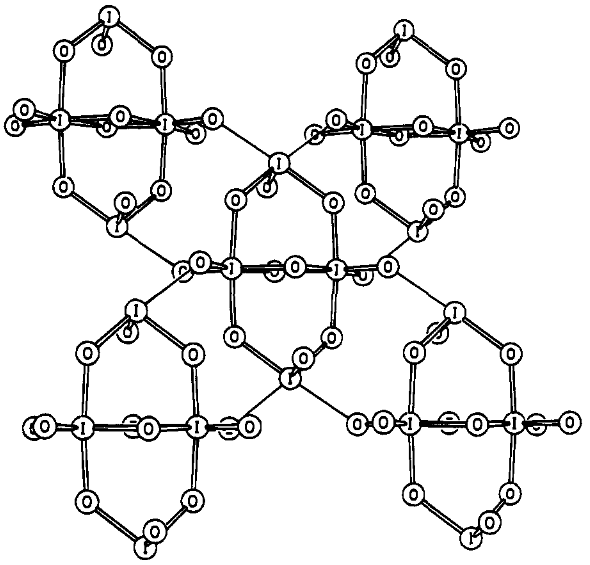

Figure 1. Section of a layer of iodine trioxide with I_4O_{12} units.

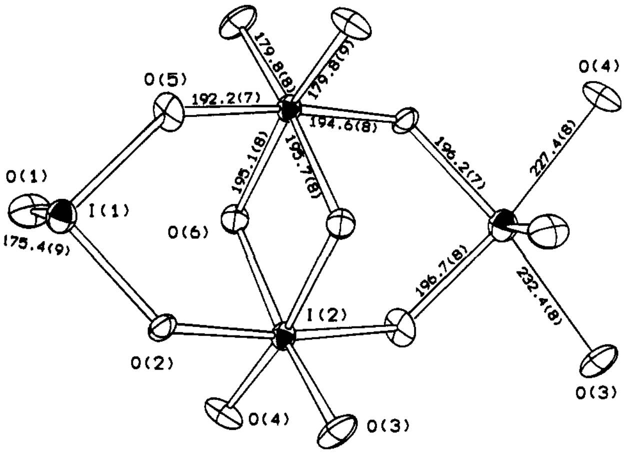

Figure 2. ORTEP representation of the I_4O_{12} unit with two intermolecular contacts and bond lengths in picometers.

The basic molecular unit I_4O_{12} can be viewed as being constructed by two IO_6 octahedra that have one edge in common and two pyramidal IO_3 units that share two of their vertices with the axial positions of the double octahedron. By their peculiar coordinations, two octahedrally coordinated iodine atoms per unit are clearly identified as being in the oxidation state +VII, while the two remaining trigonal pyramidal ones are in the +V state. Thus, the I_4O_{12} unit can be regarded as the mixed anhydride of two molecules each of H_5IO_6 and HIO_3. The site symmetry of I_4O_{12} is C_i, and within the experimental error the point symmetry is C_{2h}.

Strong intermolecular connections between the terminal equatorial oxygen atoms attached to I^{VII} and the pentavalent

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(1) Selte, K.; Kjekshus, A. *Acta Chem. Scand.* **1970**, *24*, 1912–1924.

(2) Preparation and spectroscopic characterization, (a) $ClOClO_2$: Müller, H. S. P.; Willner, H. *Inorg. Chem.* **1992**, *31*, 2528–2534. (b) Cl_2O_4: Schack, C. J.; Pilipovich, D. *Inorg. Chem.* **1970**, *9*, 1387–1390. Crystal structure determination and spectroscopic characterization, (a) ClO_2: Rehr, A.; Jansen, M. *Angew. Chem.* **1991**, *103*, 1506–1508; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1510–1512; *Inorg. Chem.* **1992**, *31*, 4740–4742. (b) Cl_2O_6: Tobias, K. M.; Jansen, M. *Angew. Chem.* **1986**, *98*, 994–995; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 993–994; *Z. Anorg. Allg. Chem.* **1987**, *550*, 16–26. Tobias, K. M.; Jansen, M.; Willner, H. *Naturwissenschaften* **1986**, *73*, 734–735. Crystal structure determination, (a) Cl_2O_7: Simon, A.; Borrmann, H. *Angew. Chem.* **1988**, *100*, 1386–1388; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1339–1341. (b) Br_2O_3: Kuschel, R.; Seppelt, K. *Angew. Chem.* **1993**, *105*, 1734–1735; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1632–1633. (c) Br_2O_5: Leopold, D.; Seppelt, K. *Angew. Chem.* **1994**, *106*, 1043–1044; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 975–976.

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(5) Siebert, H.; Weise, M.; Woerner, U. *Z. Anorg. Allg. Chem.* **1977**, *432*, 136–140.

(6) H_5IO_6 (17.5 g) (purum, p.a. Fluka) is dissolved in 50 mL of concentrated H_2SO_4 (95–97%, p.a. Riedel-de Haën). The solution is kept at 70 °C in a capped glass tube. After several days, the colorless solution becomes slightly yellow and oxygen is generated slowly. IO_3 precipitates out of this solution in yellow crystalline crusts. The reaction is completed after approximately 1 month, when the evolution of oxygen stops, and the liquid becomes colorless again. The solid is filtered off, washed three times with trifluoracetic acid, both under dry argon, and dried in vacuo at ambient temperature. Lanceolate single crystals suitable for crystal structure analysis were obtained likewise out of a solution of 3 g of H_5IO_6 in 10 mL of concentrated H_2SO_4.

(7) $P\bar{1}$ (No. 2), $V = 216.8(2)$ Å^3, Mo Kα ($\lambda = 0.710\,73$ Å) $\mu = 14.44$ mm^{-1}, $\varrho_{calc} = 5.36$ g cm^{-1}, $\varrho_{meas} = 5.401$ g cm^{-1}, $a = 5.006(2)$ Å, $b = 6.741(3)$ Å, $c = 6.795(3)$ Å, $\alpha = 97.31°$, $\beta = 96.43°$, $\gamma = 105.36°$, $Z = 1$, 1754 reflections ($F > 2\sigma(F)$) used for refinement of 73 least-squares parameters, $R = 0.064$. Sheldrick, G. M. *SHELXS-86*, *SHELXL-93*, *Programs for Crystal Structure Analysis*; Göttingen, 1986, 1993.

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iodine atoms give the crystal structure of iodine trioxide a polymeric character. The intermolecular bonds are longer than the intramolecular bridging bonds by 18% and shorter by 35% than the van der Waals contact distance of iodine and oxygen. These additional bonds increase the coordination of I^V toward a ψ-octahedron. This tendency seems to be intrinsic to the crystal chemistry of iodine(V)−oxygen systems,[8] but the intermolecular bonds in IO_3 are remarkably short. Regarding the terminal I−O bonds in one I_4O_{12} unit as double bonds and the intramolecular bridging I−O bonds as single bond, the I^{VII} parts have the formal charge of −1, and the I^V parts, +1. The short intramolecular I−O bonds compensate this formal electron defiency on I^V and the electron surplus on I^{VII}, respectively. The sterically active lone pair of I^V occupies the site opposite to the terminal oxygen atom. This is proved by the distance of 338.4(10) pm of I^V to O(1) of the adjacent layer.

These results and our knowledge about the related compounds I_2O_5,[1] I_2O_4,[9] $(IO)_2SO_4$,[10] and $I_3O_6HSO_4$[11] give an insight into the underlying principles of the iodine−oxygen chemistry: we encounter a strong tendency to form mixed odd-valency states of iodine and polymeric networks. These features explain the vast variety of possible structures and the complexity of these systems.

Acknowledgment. This work was received support by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft.

Supplementary Material Available: Tables of experimental details, atomic parameters, and bond lengths and angles (3 pages); tables of observed and calculated structure factors (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA950909V

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