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Crystal Structure Determination of Metaperiodic Acid, HIO₄, with Combined X-Ray and Neutron Diffraction**

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Dedicated to Professor Dieter Seebach on the occasion of his 60th birthday

According to textbooks on inorganic chemistry the system of iodine(VII) acids consists of the monomeric orthoperiodic acid, H₅IO₆, from which a series of oligomeric compounds $H_{6+n}I_{2+n}O_{10+4n}$ can be derived by edge-sharing of the IO₆ octahedra, and, as a terminating link, polymeric metaperiodic acid, HIO_4 .^[1] Besides the crystal structure of H_5IO_6 , which is wellestablished (including the hydrogen-atom positions),^[2] the proposed constitutions of iodine(VII) acids are based on insufficient experimental data. For the oligomeric periodic acids the I-O substructures of their salts are assumed to be similar to those of the free acids,^[3] and in the cases of HIO₄ and H₇I₃O₁₄ polymeric or trimeric chains, respectively, of trans-edge-sharing IO₆ octahedra are proposed based on Raman spectra.^[4] Attempts to grow single crystals of HIO₄ failed until now, because the compound decomposes at normal pressure, already at 105 °C, releasing oxygen and water. The development of X-ray and neutron diffraction techniques for ab initio crystal structure determination has encouraged us to investigate the structure of HIO_4 with these methods.

Microcrystalline HIO₄ was prepared by carefully dehydrating H_5IO_6 with oleum in H_2SO_4 at 50 °C. Since the reaction conditions cause the product to precipitate slowly from the homogeneous solution, the samples crystallize well despite the relatively low reaction temperature, as seen from their X-ray powder diagrams (Figure 1). The crystal structure with respect to the positions of iodine and oxygen atoms could be solved from the



Figure 1. Observed (dotted line) and calculated (solid line) diffraction diagrams and difference profile of the Rietveld refinement (top: X-ray data; bottom: neutron data); the positions of allowed reflections are indicated by vertical lines.

X-ray powder diagram; the hydrogen atoms were preliminary fixed by considering crystal-chemical evidence. Because the scattering factor of iodine is considerably higher than that of oxygen and, in particular, hydrogen, neutron diffraction techniques were necessary to complement the X-ray data. Stable refinement of the position parameters of all atoms was achieved, and the agreement between the parameter sets is satisfactory (Table 1).

Table 1. Positional parameters for HIO₄.

		x	у	Ζ.
H [a]	[b]	0.2163(28)	0.7305(47)	0.4809(67)
I	[c]	0.0	0.1432(03)	0.75
	[b]	0.0	0.1357(24)	0.75
01	[c]	0.6335(08)	0.1654(19)	0.3988(21)
	[b]	0.6258(10)	0.1637(13)	0.3934(17)
O2	[c]	0.1116(10)	0.0946(15)	0.4479(22)
	[b]	0.1122(08)	0.0935(14)	0.4506(18)

[a] Site occupancy of 50%. [b] From neutron diffraction data. [c] From X-ray diffraction data.

In contrast to all previously proposed structures, HIO_4 consists of one-dimensional infinite chains built up of distorted, *cis*-edge-sharing IO₆ octahedra (Figure 2). The different I–O distances of the IO₆ octahedra reflect the different crystal-chemical situations of the oxygen atoms (Figure 3). The terminal oxygen atoms show, as expected, the shortest I–O distances (184 pm). The pronounced difference between the distances to the bridging oxygen atoms (191 and 201 pm) can be easily explained in terms of the *trans* effect.

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Figure 2. Chains of cis-edge-sharing IO₆ octahedra.



Figure 3. IO_6 octahedron; distances are given in pm.

The structural analogy to many transition metal tetrahalides, as indicated by the presence of chains of *cis*-edge-sharing octahedra, also extends on the arrangement of these structural units relative to each other. When considering the I–O substructure, isotypism to uranium tetraiodide becomes evident, that is, the oxygen atoms form a hexagonal close packing with the iodine atoms occupying a quarter of the octahedral holes.

Every polymeric chain is connected to four adjacent chains through hydrogen bonds (Figure 4; $d(O \cdots O)$ 269(2) pm,



Figure 4. Connectivities between the chains through hydrogen bridges.

d(O-H) 101(3) pm, $d(O \cdots H)$ 169(3) pm, \star I-O-H 112(1)°, $\star O-H \cdots O$ 176(1)°). The hydrogen atoms are disordered in a double potential between the terminal oxygen atoms. This is frequently observed for linear hydrogen bonds between neutral molecules, such as in the Ih modification of ice.^[7]

Until now no periodate derived from the structure of HIO_4 —that is, built up by polymeric iodine–oxygen chains—is known. The structure of HIO_4 raises questions about the linkage of the iodine–oxygen polyhedra in oligomeric periodic acids. However, the crystal structure of $H_7I_3O_{14}$ does not show any new type of catenation, because this compound exists in the solid state as a stoichiometric phase containing orthoperiodic and metaperiodic acids according to the formula $H_5IO_6 \cdot 2HIO_4$.^[8]

Experimental Section

 HIO_4 : Oleum (25%, 15 mL) was slowly added to a solution of H_3IO_6 (3 g) in concd H_2SO_4 (40 g) at 50 °C until an insoluble precipitate appeared. Upon standing for 12 h at 50 °C a voluminous precipitate separated, which was isolated by filtration under an inert-gas atmosphere. It was treated with concd H_2SO_4 (15 mL), washed with trifluoroacetic acid (5 × 15 mL) to remove traces of H_2SO_4 , and finally dried in vacuo. Elemental analysis: iodine: 65.5% (calcd 66.1%), active oxygen: 27.9% (calcd 29.2%), sulfate: not detected.

Structure determination of HIO₄: After indexing [9] the X-ray powder diagram (Stoe Stadi P, Cu_{Ka} radiation, $\lambda = 154.051$ pm) on the basis of a monoclinic system $(a = 936.88(5), b = 629.59(4), c = 495.30(3) \text{ pm}; \beta = 94.953(3)^{\circ}), Cc \text{ (no. 9) and}$ C2/c (no. 15) were considered as possible space groups from the systematic absences. In both space groups the iodine- and oxygen-atom positions were determined with direct methods [10], but a crystal-chemically consistent refinement (156 reflections, 30 parameters, R = 0.0617, $R_{wp} = 0.219$, $R_F = 0.0522$ [11]) could only be achieved in the space group C2/c. The hydrogen bridges and, thus, the approximate positions of the hydrogen atoms were derived from crystal-chemical considerations. To verify these results optimized structure models (space group $C^{2/c}$ with disordered H atoms and Cc with no disordering of H atoms) were refined on the basis of neutron diffraction data (λ determined to 112.704 pm [11], two-circle neutron diffractometer SV7 equipped with a linear position-sensitive JULIOS detector from the Mineralogisches Institut der Universität Bonn at the reactor FRJ2 of the KFA Jülich). The model with space group C2/c was unambiguously the correct one (a = 936.60(18), b = 628.86(13), c = 495.75(19) pm; β = 94.890(15)°; 282 reflections, 27 parameters, R = 0.0185, $R_{wp} = 0.336$, $R_{F} = 0.21$ [11]).

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Ge⁴⁻: A Deltahedral Zintl Ion Now Made in the Solid-State^{**}

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All known main group deltahedral clusters are made either by crystallization from solution or by direct synthesis from the elements, that is by solid-state reactions. (We exclude gaseous clusters here since they are not structurally well characterized.) Members of the first group belong to the well known class of Zintl ions and include anions of group 14 (the tetrels (Tt): Tt_9^{-} ,

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