[7] This is confirmed by X-ray analyses of **3** and several analogous derivatives.

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[9] **7**: triclinic, space group $P\bar{1}$; $a = 11.294(7)$, $b = 13.009(9)$, $c = 18.967(12)$ Å, $\alpha = 94.770(2)$, $\beta = 98.823(1)$, $\gamma = 112.285(2)°$; $V = 2518(3) \times 10^{-6}$ pm^3; $Z = 2$, Mo$_{K\alpha}$ radiation, $2\Theta_{max} = 46.5°$, 8247 reflections, 6294 independent ($R_{int.} = 0.0412$), direct methods; refinement against full matrix (versus F^2) with SHELXTL (Version 5.0), $R_1 = 0.065$, w$R_2 = 0.1258$ (based on F^2) for 626 parameters and 4213 reflections with $I > 2\sigma(I)$. **8**: orthorhombic, space group $Pcca$ (No. 54); $a = 23.853(2)$, $b = 12.709(1)$, $c = 23.874(2)$ Å, $V = 7237.3(10) \times 10^{-6}$ pm^3, $Z = 4$, Mo$_{K\alpha}$ radiation, $2\Theta_{max} = 41.2°$, 27343 reflections, 3815 independent (R$_{int.} = 0.0880$), direct methods, refinement against full matrix (versus F^2) using SHELXL96, $R_1 = 0.046$, w$R_2 = 0.1252$ (based on F^2) for 448 parameter and 3815 reflections with $I > 2\sigma(I)$. All non-hydrogen atoms in **7** and **8** were refined with anisotropic, hydrogen atoms at calculated positions with common isotropic parameters (riding model). In addition to the complex **7**, a THF molecule, and additional electron density were localized, probably due to the presence of further disordered solvent molecules corresponding to about six C atoms. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-100707 and CCDC-101085. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Novel Bonding of Iodine: Crystal Structure of HIS_2O_8**

Martin Jansen* and Ralph Müller

Dedicated to Professor Achim Müller on the occasion of his 60th birthday

Ternary oxides of nonmetals are either ionic crystals with complex cations and anions or polymeric networks with oxygen as bridging atom, depending on the extent to which oxide ions are transferred from the acidic binary oxide to the more basic oxide. The polymeric networks are usually regarded as mixed anhydrides of oxoacids of the corresponding nonmetals, and their constitutions can be described in terms of known oxo anions as structural increments. The title compound contains the structural increment IO_2, for which neither the corresponding free acid nor the corresponding free anion is known.

The system $IO_x/SO_3/H_2O$ is very complex and only rudimentarily understood.[1] The difficulty in isolating pure crystalline phases is attibuted to their polymeric nature and thermal instability. By carefully controlling the reaction conditions, especially the duration of crystallization, compounds of this system can be prepared reproducibly in amounts of up to one gram.[2] The essential role of crystallization time is due mainly to changes in the composition of the reaction mixture during the crystallization of the product phases, and less to kinetic control of product formation. The title compound crystallizes from concentrated solutions of iodic acid in oleum under conditions similar to those described for the synthesis of $(IO_2)_2S_2O_7$ (see Experimental Section).

The composition of the title compound, including its hydrogen content, was confirmed by a single-crystal structure determination and by vibrational spectroscopy (Table 1).[3]

Table 1. IR and Raman data for HIS_2O_8 [cm^{-1}].

IR	433(w)	455(w)	573(s)	613(w)	643(w)	738(w)	851(m)
	886(m)	1008(m)	1069(s)	1231(s)	1293(s)	2479(w)	2603(w)
	2895(m)						
Raman	102(s)	139(w)	162(w)	188(m)	205(m)	240(w)	278(s)
	305(s)	457(w)	513(m)	578(w)	639(vs)	744(m)	813(w)
	870(m)	899(m)	928(w)	1001(w)	1090(m)	1149(w)	1308(w)

The constitution of the trinuclear unit $I(SO_4)(HSO_4)$ can be understood as the condensation product of one unit of sulfuric acid and one unit of hydrogensulfate with the protonated form of the hypothetical iodic(III) acid $H_2IO_2^+$. The result is a zwitterion with a positive formal charge on the iodine center and a negative charge on the the nonprotonated sulfate group (Figure 1). The S–O distances and angles have a wide range of values, but their mean values lie in the range expected for sulfates and hydrogensulfates. Both intramolecular I–O distances correspond to single-bond lengths, and the environment of the iodine(III) center can be described as ψ^2 tetrahedral.[4]

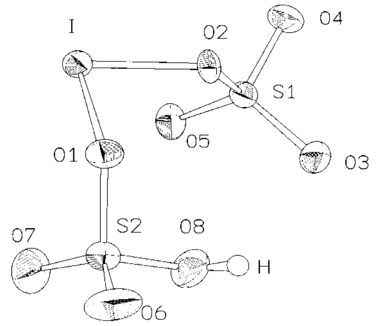

Figure 1. Structure of the trinuclear unit $I(SO_4)(HSO_4)$. Selected bond lengths [pm] (50% probability ellipsoids): I–O1 198.1(6), I–O2 197.0(6), S1–O2 158.5(6), S1–O3 145.3(7), S1–O4 147.2(7), S1–O5 140.7(7), S2–O1 157.9(6), S2–O6 140.9(9), S2–O7 139.2(8), S2–O8 151.9(8), O8–H 81.0(102).

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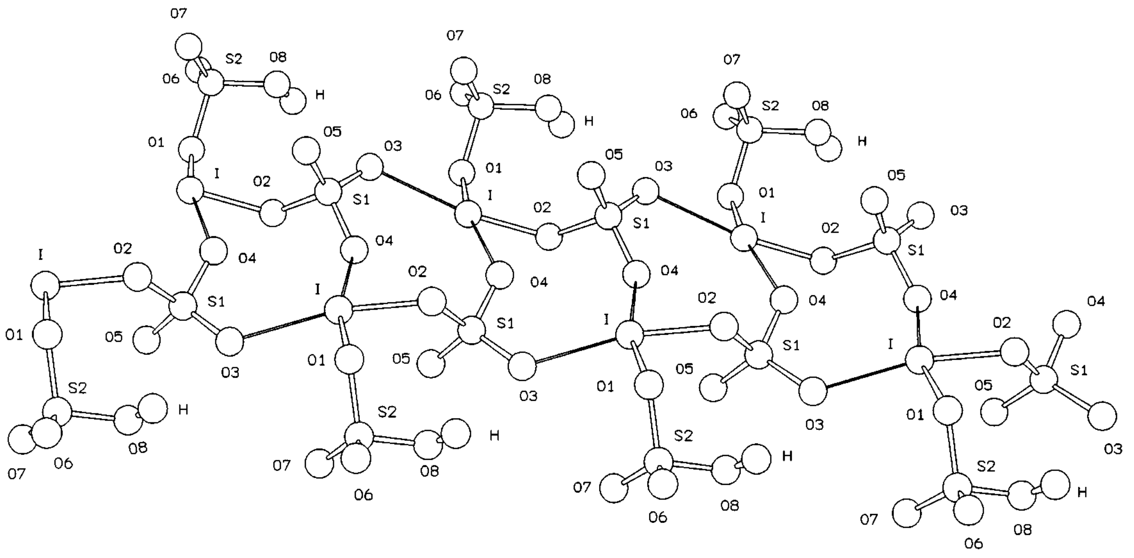

Figure 2. View of a polymeric ribbon in HIS_2O_8. The ribbons are interconnected by hydrogen bonds to form layer packages. Selected bond lengths [pm] and angles [°]: I–O3 242.4(7), I–O4 232.8(6); O1-I-O2 85.5(3), O1-I-O3 79.9(3), O1-I-O4 164.9(3), O2-I-O3 165.0(2), O2-I-O4 79.5(2), O3-I-O4 115.2(2).

The twofold coordination of the iodine center is supplemented by two oxygen atoms of two different neighboring sulfate groups to give a ψ^2 octahedrally distorted square-planar environment. However, these I–O bonds are considerably longer (233 and 242 pm) and lie between single bonds (202 pm) and van der Waals contacts (350 pm). These intermolecular interactions connect the primary units to form ribbons (Figure 2). The ribbons are interconnected by hydrogen bonds to give isolated layer packages. The variations in the I–O bond lengths can be easily understood in terms of the crystal chemical functions of the atoms involved. The shortest S–O bonds are those to the terminal oxygen atoms O5 and O7 and to O6, which acts as a hydrogen-bond acceptor. Bonds of intermediate length are formed with the O3 and O4, and the longest bonds with O8 (OH group) and with O1 and O2, which serve as bridges between iodine atoms. This gradation can be quantified by the partial valence sums.[5] The contributions of the two oxygen atoms O3 and O4 in the second coordination shell of iodine to the valence sum of iodine are strikingly low (O3 0.34, O4 0.43; Table 2).

Table 2. Calculation of the valence sums for HIS_2O_8.[5]

v_{ij}	O1	O2	O3	O4	O5	O6	O7	O8	Σv_{ij}
I	1.11	1.14	0.34	0.43					3.02
S1		1.11	1.58	1.50	1.79				5.98
S2	1.12					1.78	1.87	1.32	6.09
H								0.90	
$\Sigma v_{ij(O)}$	2.23	2.25	1.92	1.93	1.79	1.78	1.87	2.22	

$R_{ij}(I) = 202.0$, $R_{ij}(S) = 162.4$, $R_{ij}(H) = 76.1$.

Thus, the iodine atoms connecting two sulfate tetrahedra participate in novel bonding, which is best compared to that in IF_2^+ or in the monomeric S2.

Experimental Section

All preparations were performed under purified dry argon. Preparation of HIS_2O_8: iodic acid (5 mmol, purum p.a. > 99 %, Fluka) was added to oleum (100 mmol, purum p.a., Riedl-de Haën, ca. 20% SO_3) in a pear-shaped flask. The reaction mixture was heated to 210 °C over 30 min until oxygen was evolved, stirred at this temperature for a further 30 min, and then cooled to room temperature without stirring over 2 h to allow crystallization. The colorless crystals were collected by filtration, washed three times with trifluoroacetic acid (freshly distilled from P_4O_{10}), and dried in vacuo.

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