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Redetermination of HI_3O_8, an adduct of formula $HIO_3{\cdot}I_2O_5$

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Key indicators

Single-crystal X-ray study
T = 299 K
Mean σ(I–O) = 0.002 Å
R factor = 0.020
wR factor = 0.044
Data-to-parameter ratio = 18.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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Crystals of commercial iodic(V) acid, HIO_3, were investigated using single-crystal and powder X-ray diffraction. The crystals turned out to be HI_3O_8 or $HIO_3{\cdot}I_2O_5$ [iodic acid–diiodine pentaoxide (1/1)] instead, whose structure has been determined previously [Feikema & Vos (1966). *Acta Cryst.* **20**, 769–777]. Redetermination of the structure gave higher precision and allowed the location of the H atom.

Comment

The structures of the oxoacids of iodine(V) have been investigated extensively. Two polymorphs of iodic acid, HIO_3, are known. The stable polymorph, α-HIO_3, has been characterized several times, using both X-ray and neutron diffraction methods (Rogers & Helmholtz, 1941; Ståhl & Szafranski, 1992*a*,*b*). Recently, we were able to determine the structure of a metastable polymorph, γ-HIO_3, whereas the existence of the β polymorph is doubtful (Fischer & Lindsjö, 2005). An additional compound in the system I_2O_5/H_2O is the adduct $HIO_3{\cdot}I_2O_5$, (I). Its structure was established previously by Feikema & Vos (1966). While the overall results of that structure determination are beyond doubt, the position of the H atom could be determined only indirectly.

It therefore appeared desirable to perform a new structure determination of (I), the results of which are presented here. The redetermination has improved the precision of the structure significantly and made it possible to locate the H atom in a difference Fourier map.

The basic structural unit of (I) is displayed in Fig. 1. The result essentially confirms the geometry of both the I_2O_5 and the HIO_3 moieties. The I atoms in the I_2O_5 moiety possess rather distorted octahedral coordinations, with three short I—O bonds and three rather long I···O contacts (see Table 1). Atom I3 in the HIO_3 moiety has two such I···O contacts, yielding a fivefold coordination (Fig. 2).

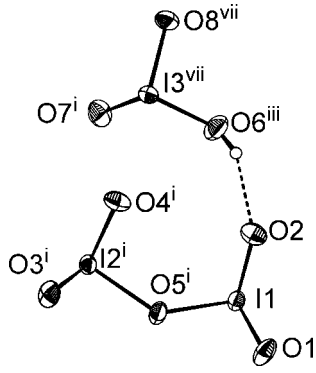

Figure 1
The HIO_3 and the I_2O_5 units in the structure of HI_3O_8. Displacement ellipsoids are drawn at the 80% probability level. [Symmetry codes are as in Table 1; additonally, (vii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.]

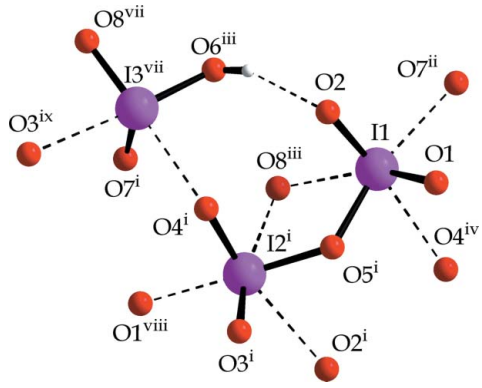

Figure 2
The distorted octahedral coordination of the I atoms in HI_3O_8. Solid lines indicate I—O bonds and dashed lines indicate I···O contacts. [Symmetry codes as in Table 1; additionally, (vii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (viii) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$; (ix) $x-\frac{1}{2}, \frac{3}{2}-y, \frac{1}{2}+z$.]

In the previous structure determination (Feikema & Vos, 1966), the position of the H atom in (I) was derived indirectly from geometric and crystallochemical considerations. It was suggested to be bonded to atom O6, forming a hydrogen bond with atom O2. In the present structure determination, a distinct electron-density maximum could be found in a difference Fourier synthesis, thus confirming the structural model that had been suggested previously. The hydrogen-bonding geometry is presented in Table 2.

Experimental

Crystals selected from commercial iodic acid (Alfa Aesar, 99.5%) were used as purchased. Powder X-ray diffraction of the bulk material revealed *ca* 90% HI_3O_8 and 10% α-HIO_3.

Crystal data

$HIO_3{\cdot}I_2O_5$
$M_r = 509.71$
Monoclinic, $P2_1/n$
$a = 7.5529\ (4)$ Å
$b = 7.6961\ (4)$ Å
$c = 11.3787\ (5)$ Å
$\beta = 90.178\ (4)^\circ$
$V = 661.42\ (6)$ Å^3
$Z = 4$
$D_x = 5.120$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 108 reflections
$\theta = 5.6$–23.0°
$\mu = 14.18$ mm^{-1}
$T = 299$ K
Fragment, colourless
0.23 × 0.17 × 0.16 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: numerical (*HABITUS*; Herrendorf & Bärnighausen, 1997)
$T_{min} = 0.189$, $T_{max} = 0.355$
12999 measured reflections
1913 independent reflections
1847 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$
$\theta_{max} = 30.0^\circ$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -15 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.044$
$S = 1.27$
1913 reflections
101 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0157P)^2 + 1.6864P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.78$ e Å^{-3}
$\Delta\rho_{min} = -1.49$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0185 (4)

Table 1
Selected bond lengths (Å).

I1—O2	1.782 (3)	I2—O1^{ii}	2.390 (2)
I1—O1	1.789 (3)	I2—O8^{v}	2.569 (3)
I1—O5^{i}	1.953 (3)	I2—O2	2.829 (3)
I1—O7^{ii}	2.575 (2)	I3—O7^{iv}	1.790 (3)
I1—O8^{iii}	2.636 (2)	I3—O8	1.792 (3)
I1—O4^{iv}	2.712 (3)	I3—O6^{vi}	1.880 (3)
I2—O3	1.788 (3)	I3—O3^{ii}	2.545 (3)
I2—O4	1.794 (3)	I3—O4^{iv}	2.593 (3)
I2—O5	1.952 (2)		

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+1, -y+1, -z$; (iii) $x-1, y, z$; (iv) $x, y-1, z$; (v) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (vi) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O6—H6···O2^{vii}	0.80	2.00	2.744 (4)	156

Symmetry code: (vii) $x+1, y, z$.

The result of the previous structure determination (Feikema & Vos, 1966) was used as a starting model. The H atom was located in a difference Fourier synthesis. It was refined as riding, with $U_{iso}(H) = 1.2U_{eq}(O6)$. The highest difference peak is located 0.88 Å from I3, and the deepest hole is 0.80 Å from the same atom. The precision of the structure was improved significantly (the s.u. values of the bond lengths decreased by a factor of 3). Although the atoms in this description do not form a single connected set without the use of several symmetry operators (as seen in Fig. 1), we have retained it for comparison with the original report, in which all atom coordinates were kept within the range 0–1.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: coordinates taken from previous determination; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *MAXUS* (Mackay *et al.*, 1999).

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