# $\gamma$ -HIO<sub>3</sub> – a Metastable, Centrosymmetric Polymorph of Iodic Acid

# Andreas Fischer\* and Martin Lindsjö

Stockholm / Sweden, Inorganic Chemistry, Royal Institute of Technology (KTH)

Received March 3rd, 2005.

**Abstract.** From solutions of chromium(III) perchlorate and periodic acid, single crystals of  $\gamma$ -HIO<sub>3</sub> were obtained and characterized by single-crystal X-ray diffraction, Raman spectroscopy and thermal analysis. The compound crystallizes in the orthorhombic crystal system, space group *Pbca* (a = 563.92, b = 611.10, c = 1507.16 pm). The structure is built up by dimers (HIO<sub>3</sub>)<sub>2</sub>, which

are formed by hydrogen bonds. The crystals are metastable and transform into the stable modification,  $\alpha$ -HIO<sub>3</sub>, within a couple of weeks.

Keywords: Iodic acid, Polymorphism

#### Introduction

Iodic acid and oxoiodates(V) have been object of research for a long period of time. This is due to the interesting optical properties of the acid itself, which is being used for second harmonic generation [1], and the potential similar properties of salts derived from this acid. The structure of iodic acid is therefore well investigated. It was for the first time determined in 1941 [2] and was investigated more thoroughly on a later occasion [3, 4]. Iodic acid crystallizes in the non-centrosymmetric space group  $P2_12_12_1$ , which apparently is a prerequisite of the exceptional optical properties. The structure is built by hydrogen-bonded chains of HIO<sub>3</sub> molecules. There is some evidence in the literature of a possible polymorphism of iodic acid [5 and references therein]. However, no structural characterization of a second polymorph has been described so far.

In our investigation of different transition metal/periodate systems, we have studied mixtures of solutions of chromium(III) perchlorate and periodic acid. In these mixtures, chromium(III) is rapidly oxidized to chromium(VI). Upon evaporation of one of these solutions, single crystals of the title compound could be isolated. The compound was characterized by single-crystal X-ray diffraction and Raman spectroscopy and the results are presented here.

#### **Results and Discussion**

A reaction mixture of chromium(III) perchlorate and an excess of iodic acid yielded immediately a yet unidentified chromium(VI) species. Upon evaporation, the reduction

product of  $H_5IO_6$ ,  $HIO_3$ , crystallized as thin, hexagonal, slightly elongated plates. A determination of the lattice constants on the single-crystal diffractometer showed that the structure was not represented in the ICSD. We therefore decided to perform a characterization, using single-crystal X-ray diffraction and Raman spectroscopy. Additionally, we attempted to study the thermal behaviour.

Details of the single-crystal structure determination are given in Table 1, Table 2 lists the atomic parameters, Table 3 some important interatomic distances and bond angles.  $\gamma$ -HIO<sub>3</sub> crystallizes in the orthorhombic space group *Pbca*.

**Table 1** Crystallographic data and results of the structure determination of  $\gamma$ -HIO3. Standard deviations are given in parantheses.<sup>a)</sup>

	γ-HIO <sub>3</sub>
Sum formula	HIO <sub>3</sub>
Lattice constants/pm	a = 563.92(3)
	b=611.10(4)
	c = 1507.16(9)
Cell volume/106 pm3	519.38(5)
density (calc.)/g·cm <sup>-3</sup>	4.50
formula weight	175.91
number of formula units	8
Crystal system, space group	orthorhombic, Pbca (No. 61)
Temperature of measurement	299 K
Diffractometer	Bruker-Nonius KappaCCD
Radiation, wavelength	Mo-Kα, 71.073 pm
absorption coefficient/cm <sup>-1</sup>	104.5
Crystal size/mm	0.01×0.10×0.15
absorption correction	numerical, T <sub>min</sub> =0.189, T <sub>max</sub> =0.886
number of reflections	5758
unique reflections, R <sub>int</sub>	588, 0.0310
number of parameters	38
Extinction correction	SHELXL97
Extinction coefficient	0.0021(2)
R values	$wR_2 = 0.0348^{b}$
	R=0.0215 for all reflections
	R=0.0176 for 538 reflections with I> $2\sigma(I)$
Goodness of fit	1.178
Largest electron density	0.71 / -0.57
difference peak/hole	

<sup>a)</sup> Crystallographic data for the structures have been deposited with the FIZ Karlsruhe, D-76344 Eggenstein-Leopoldshafen/Germany, e-mail **crysdata@fiz-karlsruhe.de**. Copies of the data can be retrieved free of charge by citing the deposition numbers CSD-415140. <sup>b)</sup> w=[ $\sigma^2 F_o^2 + 1.0085 P$ ]<sup>-1</sup> where P=( $F_o^2 + 2F_c^2$ )/3

<sup>\*</sup> Dr. A. Fischer Inorganic Chemistry Royal Institute of Technology (KTH) 100 44 Stockholm Sweden Phone: +46(0)8 790-7987 Fax: +46(0)8 212 626 E-mail: andif@inorg.kth.se

**Table 2** Atomic positions and equivalent isotropic displacement parameters  $B/10^4$  pm<sup>2</sup> of the atoms in the structure of  $\gamma$ -HIO<sub>3</sub>. Standard deviations are given in parentheses.

Atom	x	у	Ζ	В
I(1)	0.00770(3)	0.33394(3)	0.15461(1)	0.907(9)
O(1)	0.2483(4)	0.4788(4)	0.20725(14)	1.43(4)
O(2)	-0.1504(4)	0.5543(4)	0.10325(14)	1.56(4)
O(3)	0.1604(4)	0.2357(4)	0.05171(14)	1.56(4)
H(3)	0.1793	0.3460	0.0117	1.89

**Table 3** Selected interatomic distances and bond angles in the structure of  $\gamma$ -HIO<sub>3</sub>. Standard deviations are given in parentheses. Symmetry operations: i: -0.5-x, -0.5+y, z; ii: 0.5-x, -0.5+y, z; iii: -0.5+x, y, 0.5-z; iv: -x, 1-y, -z.

atoms	distance / pm	bonds	bond angle / °
I(1) = O(1)	180.4(2)	O(1) - I(1) - O(2)	101.3(1)
I(1) - O(2)	191.1(2)	O(2) - I(1) - O(3)	96.4(1)
I(1) - O(3)	187.3(2)	O(3) - I(1) - O(1)	100.1(1)
$I(1) - O(1^{i})$	268.9(2)	I(1) - O(3) - H(3)	111.4(2)
$I(1) - O(1^{ii})$	269.4(2)		
$I(1) - O(2^{iii})$	275.3(2)		
O(3) - H(3)	91.1(2)		
$O(2^{iv}) - H(3)$	184.4(2)		

There is one HIO<sub>3</sub> molecule in the asymmetric unit, in a position close to an inversion centre. Thus, a second molecule is generated by symmetry, which is connected to the first one by two hydrogen bonds (Fig. 1). This makes the structure remarkably different from that of the  $\alpha$  modification, where one molecule acts as an H-bond donor towards one neighbour molecule and as an acceptor towards another, yielding infinite chains. Figure 2 shows the packing of the HIO<sub>3</sub> molecules in the crystal structure.

The geometry of the HIO<sub>3</sub> molecule is essentially the same as the  $\alpha$  modification (I–O bonds: 179.1-187.3 pm;  $\alpha$ : 178.3-189.6 pm). The H bond is significantly longer than in the  $\alpha$  form (184.4 pm as compared to 172.5 pm).

In conformity with  $\alpha$ -HIO<sub>3</sub>, each iodine atom is coordinated by three oxygen atoms from neighbouring acid molecules, yielding a distorted octahedral surrounding (I–O: 268.9–275.3 pm;  $\alpha$ : 250.4–288.9 pm). The spread of the long I-O contacts is thus much larger in the stable  $\alpha$  modification. It can be noted that the density of the title compound is significantly lower than that of  $\alpha$ -HIO<sub>3</sub> ( $\alpha$ : 4.63 g/cm<sup>3</sup>,  $\gamma$ : 4.50 g/cm<sup>3</sup>).



Fig. 1 The dimer  $(HIO_3)_2$  in  $\gamma$ -HIO<sub>3</sub>. Thermal ellipsoids are drawn at the 70 % probability level. Symmetry operations: i: -0.5-x, -0.5+y, z; ii: 0.5-x, -0.5+y, z; iii: -0.5+x, y, 0.5-z.



**Fig. 2** The unit cell of  $\gamma$ -HIO<sub>3</sub> in a view along the *a* axis. The H bonds in one of the (HIO<sub>3</sub>)<sub>2</sub> dimers are indicated by dashed lines.



Fig. 3 Raman spectra, 130-1000 cm<sup>-1</sup>, of  $\alpha$ -HIO<sub>3</sub> (bottom) and  $\gamma$ -HIO<sub>3</sub> (top).

If crystals of  $\gamma$ -HIO<sub>3</sub> are set aside in the reaction medium, they transform slowly, within a couple of weeks, into the stable polymorph. Thermal investigations of  $\gamma$ -HIO<sub>3</sub> turned out to be difficult, since only very small amounts could be isolated. The calculation of transformation enthalpies was therefore not possible. DSC investigations show an exothermic reaction at 160°, which is in good agreement with previous studies [5].

In those studies, an X-ray investigation (powder diffraction) of " $\beta$ -HIO<sub>3</sub>" was undertaken. However, the diffraction data are not at all in agreement with those calculated for the title compound. Nor do the lattice constants, which were determined in our investigations, agree with the ratios given in earlier publications. We decided therefore to call our metastable polymorph " $\gamma$ -HIO<sub>3</sub>", leaving the question open whether there really is a  $\beta$  modification.

Raman spectra for solid  $\alpha$ -HIO<sub>3</sub> and  $\gamma$ -HIO<sub>3</sub> are shown in Figure 3. Raman bands observed for the two modifi**Table 4** Observed Raman bands  $/cm^{-1}$  for solid  $\alpha$ -HIO<sub>3</sub> and  $\gamma$ -HIO<sub>3</sub>. Assignments for  $\alpha$ -HIO<sub>3</sub> are taken from reference [6].<sup>a)</sup>

γ-HIO <sub>3</sub>	$\alpha$ -HIO <sub>3</sub>	Assignment [6]
	836, vw	$v_8$ + lattice mode
793, m	782, s	$v_8$ , IO <sub>2</sub> antisymmetric stretching
	763, w	$v_8$ + lattice mode
729, vs	714, s	$v_3$ , IO <sub>2</sub> symmetric stretching
674, vw	633, s	$v_4$ , IO' stretching
392, w	380, w	v <sub>5</sub> , O'IO <sub>2</sub> rocking
342, m	330, m	$v_6$ , IO <sub>2</sub> deformation
	314, sh	0, 2
	297, w	$v_0$ , O'IO bending
277. vw	,	<i>,, , , , , , , , , ,</i>
263, vw		
<i>,</i>	220, vw	Lattice mode
	194, vw	Lattice mode

a) Abbrevations: s, strong; m, medium; w, weak; sh, shoulder; v, very.

cations are listed in Table 4. The spectrum of  $\alpha$ -HIO<sub>3</sub> is in very good agreement with earlier measurements [6]. On the other hand, the spectrum of the title compound includes some apparent differences, particularly in the region of I–O stretching modes, 600-800 cm<sup>-1</sup>.

#### Conclusion

By reaction of chromium(III) perchlorate with an excess of periodic acid in aqueous solution, iodic acid was obtained. Slow evaporation of the water yielded crystals of a new, metastable polymorph of iodic acid. This finding could be reproduced in a second experiment. Apparently, the composition of the reaction system hampers the crystallization of the stable  $\alpha$  modification or leads to an increased formation of dimers (HIO<sub>3</sub>)<sub>2</sub> in solution, which favours the crystallization of  $\gamma$ -HIO<sub>3</sub>.

#### **Experimental Section**

A 1-molar solution of chromium(III) perchlorate was prepared from "Cr(ClO<sub>4</sub>)<sub>3</sub>·6 H<sub>2</sub>O" (Alfa Aesar) and demineralized water. As was determined later, this hydrate is really a nonahydrate. The chromium concentration was thus slightly lower than initially calculated. 0.262 g of this solution were mixed with 0.855 g of a 1-molar solution of periodic acid (Aldrich, 99.999 %). The colour of the solution turned instantaneously to orange. The solution was kept in normal laboratory atmosphere in an open NMR tube for evaporation. After a couple of months, thin hexagonal colourless plates of  $\gamma$ -HIO<sub>3</sub> were obtained. These transformed into the stable  $\alpha$ modification within a couple of weeks.

#### Structure determination

Details of the structure determination are listed in Table 1.

Diffraction data were collected on a Bruker-Nonius KappaCCD diffractometer. Numerical absorption corrections were applied [7]. A structure model, consisting of I and O atoms, was obtained using direct methods [8]. The structure was refined on  $F^2$  with anisotropic displacement parameters for all atoms [9]. The hydrogen atom was then localized in a difference-Fourier synthesis and refined using a riding model. All figures were prepared using DIAMOND [10].

### Raman spectroscopy

Raman spectra from single crystals of  $\alpha$ -HIO<sub>3</sub> and  $\gamma$ -HIO<sub>3</sub>, respectively, were recorded using a Renishaw System 1000 spectrometer, equipped with a DMLM Leica microscope and a 25 mW He-Ne laser (633 nm).

## DSC analysis

A sample of approximately 1 mg of  $\gamma$ -HIO<sub>3</sub> was sealed into an Al capsule. A DSC experiment was done on a PerkinElmer DSC7 differential scanning calorimeter. Due to the high uncertainty of the mass determination, no attempt was made to obtain quantitative data.

Acknowledgements. Dr. Zoltán Szabó is acknowledged for his valuable help with translations from the Hungarian. The Swedish Research Council (VR) is acknowledged for financial support.

#### References

- [1] S. K. Kurtz, T. T. Perry, J. G. Bergman Jr., Appl. Phys. Lett. 1968, 12, 186–188.
- [2] M. T. Rogers, L. Helmholz, J. Am. Chem. Soc. 1941, 63, 278-284.
- [3] K. Ståhl, M. Szafranski, Acta Chem. Scand. 1992, 46, 1146–1148.
- [4] K. Ståhl, M. Szafranski, Acta Crystallogr. 1992, C48, 1571–1574.
- [5] A. Halász, A, Jánosi, K., Lábdy, Veszpremi Vegyipari Egyetem Kozlemenyei, 1960, 4, 159–168.
- [6] J. R. Durig, O. D. Bonner, W. H. Breazeale, J. Phys. Chem. 1965, 69, 3886-3892.
- [7] W. Herrendorf, H. Bärnighausen: HABITUS a program for numerical absorption correction, Universities of Giessen and Karlsruhe, Germany, 1997.
- [8] G. M. Sheldrick, SHELXS97, a program for crystal structure solution, University of Göttingen, Germany, 1997.
- [9] G. M. Sheldrick, SHELXL97, a program for crystal structure refinement, University of Göttingen, Germany, **1997**.
- [10] DIAMOND 2.1e. Crystal Impact GbR, Bonn, Germany, 2001.