Crystal structure of a new polymorph of iodic acid, δ-HIO_3, from powder diffraction

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A new polymorph of iodic acid, δ-HIO_3, synthesized via aerosol spray pyrolysis was characterized with powder X-ray diffraction and its crystal structure was solved. We find that a previously misidentified phase of I_4O_9 hydrate is in fact a new polymorph of HIO_3, which crystalizes in the orthorhombic space group $P2_12_12_1$. © *2017 International Centre for Diffraction Data*.
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Key words: iodic acids, crystal structure determination, powder diffraction, I_4O_9 hydrate, Rietveld refinement

I. INTRODUCTION

As one of the iodates (MIO_3, where $M = H^+$, NH^{4+}, alkali ions, etc.), HIO_3 has been of interest because of its potential application as an optically non-linear material (Bergman *et al*., 1969; Naito and Inaba, 1972; Stahl and Szafranski, 1992). The crystal structure of α-phase of iodic acid was first reported in 1941, and crystalizes in the orthorhombic space group D_2^4-$P2_12_12_1$ (Rogers and Helmholz, 1941). The structure is held together by hydrogen bonds and relatively weak intermolecular iodine oxygen bonds. More recently, neutron powder diffraction at various temperatures were able to more precisely determine the position of hydrogen atoms in the crystal structure (Stahl and Szafranski, 1992). Decreased intermolecular distances and O–I–O angles of α-HIO_3 were observed with decreasing temperature. In 2005, a new metastable, centrosymmetric polymorph of iodic acid, γ-HIO_3, was obtained via reaction between H_5IO_6 and $Cr(ClO_4)_3$ in aqueous solution, which crystalizes in the orthorhombic space group *Pbca*. This phase is stabilized by hydrogen-bonded $(HIO_3)_2$ dimers (Fischer and Lindsjö, 2005).

Thermal decomposition of iodic acid in air can lead to I_2O_5 or HI_3O_8 depending on temperature (Little *et al*., 2015). Gas phase aerosol techniques offer a convenient route and potentially direct route for preparation of small particles with high purity, and is a method proven to be amenable and economical to scale-up (Jang *et al*., 2013; Kaplowitz *et al*., 2013; Zhou *et al*., 2015; Liu *et al*., 2016). In our investigation of aerosol route synthesis of different iodine oxides/iodic acids using HIO_3 as the precursor solution, we found a new polymorph could be obtained with silica gels regenerated at ~50 °C and the furnace temperature at ~210 °C (Wu *et al*., 2017). Here, its crystal structure is reported for the first time.

II. EXPERIMENTAL AND STRUCTURE DETERMINATION

Iodic acid (α-HIO_3) (99.5 wt%) purchased from Sigma-Aldrich was directly used as received. All the other

TABLE I. X-ray diffraction patterns for δ-HIO_3 and I_4O_9• xH_2O (PDF#00–045–0872).

δ-HIO_3			I_4O_9• xH_2O	
$2\theta_{calc}$ (°)	d_{calc} (Å)[a]	I_{obs}[b]	d_{obs} (Å)	I_{obs}[c]
16.494	5.37	7		
21.022	4.222	100	4.19	m
23.534	3.777	66	3.75	s
24.642	3.61	11	3.59	vw
25.585	3.479	22		
25.818	3.448	13	3.46	m
28.982	3.078	4		
31.760	2.815	49	2.81	s
33.344	2.685	18	2.68	m
34.337	2.609	7	2.61	w
37.667	2.386	3	2.39	vw
39.039	2.305	4	2.31	vw
40.293	2.236	3	2.24	vw
42.797	2.111	4	2.12	vw
43.886	2.061	11	2.055	m
44.826	2.02	11	2.015	m
45.672	1.985	5	1.98	m
47.538	1.911	7	1.905	m
48.143	1.889	6	1.882	m
49.144	1.852	12	1.847	m
49.414	1.843	13	1.837	m
50.527	1.805	6	1.803	m
52.570	1.739	4	1.737	w
53.079	1.724	7	1.72	m
54.760	1.675	7	1.672	m

[a]d_{calc} – *d*-spacing calculated from lattice parameters obtained from Rietveld refinement.
[b]Normalized observed integrated intensities as obtained from the Rietveld refinement.
[c]Observed intensity denoted as m = medium, s = strong, vw = very weak, w = weak (Wikjord *et al*., 1980).

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chemicals were of analytical grade and used as purchased without further treatment.

Small-sized particles of δ-HIO_3 were obtained via aerosol spray pyrolysis (ASP). In general, 100 ml iodic acid solution (10 mg ml^{-1}) were sprayed into small droplets (~1 μm in diameter) with a homemade pressure atomizer (~35 psi pressure air) and pass through a silica-gel diffusion drier (silica gels were regenerated at ~50 °C) to remove most of the water, and are then passed through a tube furnace for chemical conversion. The tube reactor consisted of a ~1.9 cm diameter alumina tube with a heated length of ~40 cm. The furnace temperature was set at ~210 °C to obtain δ-HIO_3 with a residence time of about 1 s. We find that δ-HIO_3 can be obtained within a large range of temperature from 180 to 250 °C. The final product was collected on a Millipore membrane filter (0.4 μm pore) and characterized by powder X-ray diffraction (XRD, Bruker D8 Advance using Cu$K\alpha$ radiation).

The as-prepared samples were characterized by powder XRD. Diffraction pattern was measured using Cu$K\alpha$ radiation in Bragg–Brentano geometry on Bruker D8 Advance powder diffractometer equipped with incident beam Soller slits, Ni β-filter and LynxEye position sensitive detector. Data were collected from 14 to 130°2θ with a step size of 0.015 78° and counting time of 1 s $step^{-1}$ (total exposure time of 180 s $step^{-1}$).

The powder pattern was indexed in the orthorhombic crystal system and reflection conditions pointed to a $P2_12_12_1$ space-group symmetry. This phase matched a previously reported for I_4O_9• xH_2O (PDF#00-045-0872) (Table I). In this case "I_4O_9• xH_2O" was designated to refer to a crystal hydrate product of amorphous I_4O_9 according to the paper that published its XRD result (Wikjord *et al.*, 1980). However, the I_4O_9• xH_2O reference provides only composition and powder pattern and motivated our consideration of determining rigorously the crystal structure.

The crystal structure was solved from the integrated intensities obtained from a LeBail full pattern decomposition by a charge flipping method using an XT program from ShelX software (Sheldrick, 2015). The crystal structure (Figure 1) was refined by Rietveld method using the Topas software (Cheary and Coelho, 1992). The refinement revealed a presence of preferred orientation with a March–Dollase parameter of 0.75(1). Hydrogen atom was positioned from geometric considerations at the longest I–O bond along the shortest oxygen–oxygen contact line as it was observed in other structures of iodic acid. It was refined as riding on the attached O atom.

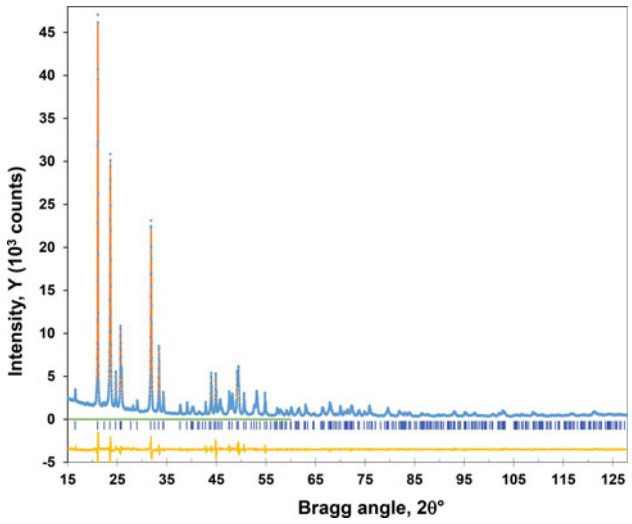

Figure 1. (Colour online) The Rietveld plot of δ-HIO_3 (circles – experimental profile, solid line – calculated, their difference is shown at the bottom, vertical lines show the reflection position).

III. DISCUSSION

This crystal structure determination shows that the actual chemical composition of I_4O_9• xH_2O is HIO_3, which could also be written as I_4O_{10}•$2H_2O$. This new polymorphic modification of iodic acid is further referred as δ-HIO_3 (CCDC#1526763).

Details of the crystal structure determination are shown in Table II. The atomic parameters are listed in Table III. Selected interatomic distances and bond angles of δ-HIO_3, α-HIO_3 (Stahl and Szafranski, 1992), γ-HIO_3 (Fischer and Lindsjö, 2005), and HI_3O_8 (Fischer, 2005) are shown in Table IV.

The δ-HIO_3 crystalizes in the orthorhombic space group $P2_12_12_1$. Figures 2(a) and 2(b) show the crystal structure of δ-HIO_3 with each iodine atom 3 coordinated with oxygen atoms (I1–O1 = 1.904, I1–O2 = 1.811, I1–O3 = 1.741), and all four atoms form trigonal pyramid with iodine atoms in the apex and three oxygen atoms in the base. One of the I–O contacts of 2.49 ÅA between molecules make spiral chain along the z direction [Figure 2(a)], and two more long I–O contacts of ~2.76 Å bind the chains in x and y directions into a three-dimensional framework [Figure 2(b)]. O1–H1…O2 hydrogen bond links HIO_3 molecules into a zig-zag chain along the y-direction, which make it unique as compared with other two polymorphs of HIO_3. Two neighboring molecules are in a mirror position along with xy-plane. Three I–O bonds and three I…O contacts together make a distorted octahedra.

All three iodic acid structures α, γ, and δ differ by packing of the HIO_3 molecules and therefore by arrangement of their hydrogen bonds. In α-HIO_3, similarly δ-HIO_3 structure, hydrogen bonds link molecules into a zig-zag chains

TABLE II. Details of the crystal structure determination of δ-HIO_3.

Formula	HIO_3
Lattice constants (Å)	a = 8.445 04(13)
	b = 6.957 85(13)
	c = 4.497 53(10)
Cell volume ($Å^3$)	264.272(9)
Density	4.421
Formula weight	175.91
Number of formula units	4
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature of measurement	Room temperature
Diffractometer	Bruker D8 Advance
Radiation, wavelength	Cu$K\alpha$ radiation, 1.5418 Å
Absorption coefficient (cm^{-1})	93.256
F000, electrons	312
Number of reflections	284
R values (%)	R_{exp} = 3.09
	R_{wp} = 6.56
	R_p = 5.10
	R_{Bragg} = 1.22
Goodness of fit	2.122

TABLE III. Atomic coordinates and isotropic displacement parameters (Å^2) of δ-HIO_3.

Atom	Site	*x/a*	*y/b*	*z/c*	B_{iso}
I1	4a	0.278 20(7)	0.230 62(12)	0.0264(2)	0.79(5)
O1	4a	0.3414(16)	0.4389(14)	0.274(3)	0.62(13)
O2	4a	0.3542(15)	0.0372(16)	0.255(3)	0.62(13)
O3	4a	0.0873(7)	0.254(2)	0.1678(16)	0.62(13)
H1	4a	0.440 511	0.444 325	0.282 977	0.92(19)

[Figure 3(a)]. However, in γ-HIO_3 hydrogen bonds form $(HIO_3)_2$ pair as shown in Figure 3(b). Figure 3(c) shows that HI_3O_8 molecule is an adduct of both HIO_3 and I_2O_5 moieties that are connected by a hydrogen bond (Fischer, 2005). Interestingly, the hydrogen bond in δ-HIO_3 structure is similar in length to γ-HIO_3 molecule and both are slightly shorter than that of α-HIO_3 and HI_3O_8 structures.

Each IO_3 pyramid forms three I...O intermolecular contacts in 2.5–3.1 Å range (Table III), which along with three I–O bonds form a distorted octahedra. Each I...O contact is positioned across I–O bond so that O–I...O angle deviates from liner for not more than 17°. This is true for all HIO_3 structures as well as HIO_3 and I_2O_5 molecules in HI_3O_8 structure. There is also correlation, at least qualitatively, between length of I–O bonds and opposite I...O contact distances: the shorter bond corresponds to longer contact and vice versa.

IV. CONCLUSION

A new polymorph of iodic acid, δ-HIO_3, which crystallizes in the orthorhombic space group $P2_12_12_1$, was obtained via a reproducible ASP method using iodic acid solution as the precursor. *Ab initio* crystal structure determination of δ-phase reveals that previously known $I_4O_9 \bullet xH_2O$ phase is actually HIO_3.

SUPPLEMENTARY MATERIAL

The supplementary material for this article can be found at https://doi.org/10.1017/S0885715617000859.

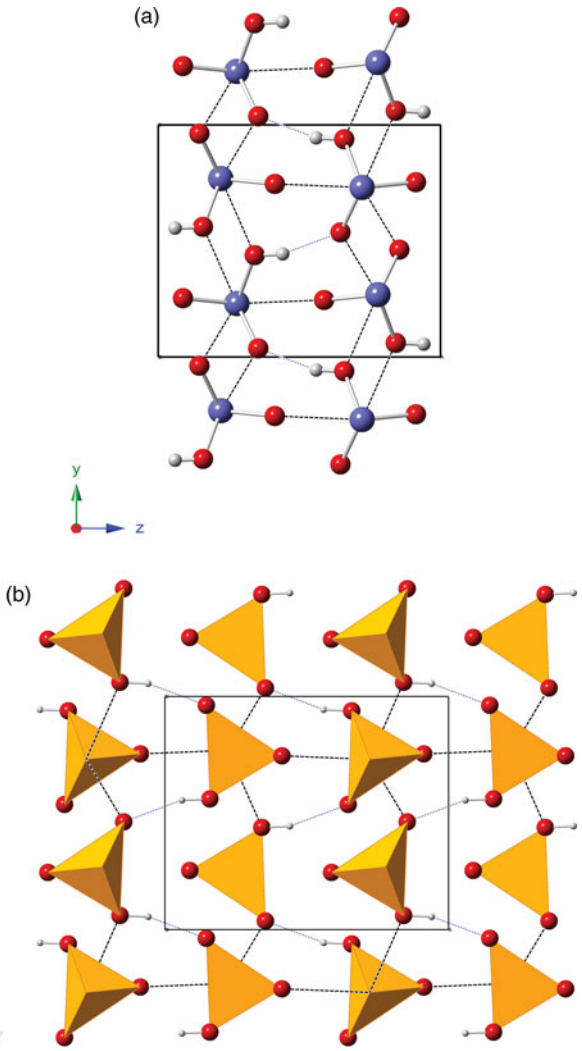

Figure 2. (Colour online) The structure of δ-HIO_3 showing: (a) a layer in *ab*-plane with chains H-bonded along *b*-axis and (b) corresponding polyhedral representation. Blue dotted lines show H...O contacts and dashed black lines show I...O contacts. Red, blue, and gray balls represent oxygen, iodine, and hydrogen atoms, respectively.

TABLE IV. Selected interatomic distances (Å) and angles (°) δ-HIO_3 in comparison to corresponding geometries of similar compounds.

	Atom labels	δ-HIO_3 (this work)	α-HIO_3	γ-HIO_3	HI_3O_8 ($HIO_3 \cdot I_2O_5$)
Distances (Å)	I1–O1	1.904(12)	1.896(2)	1.873(2)	1.880(3)
	I1–O2	1.811(12)	1.812(2)	1.791(2)	1.792(2)
	I1–O3	1.741(6)	1.783(1)	1.804(2)	1.790(3)
Valence angles (°)	O1–I–O2	97.7(5)	97.63(7)	100.1(1)	93.73(12)
	O1–I–O3	88.6(6)	93.86(6)	96.4(1)	95.07(12)
	O2–I–O3	101.0(6)	100.92(7)	101.3(1)	99.16(13)
Contacts (Å)	I1...O2[a]	2.493(12)	2.504(2)	2.694(2)	2.545(2)
	I1...O1[b]	2.757(11)	2.760(2)	2.689(2)	2.593(3)
	I1...O3[c]	2.754(6)	2.889(1)	2.753(2)	3.123(3)
Contact angles (°)	O1–I...O2[a]	168.9(5)	174.47(7)	174.26(8)	176.39(11)
	O2–I...O1[b]	169.6(5)	166.49(6)	171.49(8)	177.44(11)
	O3–I...O3[c]	171.8(5)	163.28(7)	168.17(9)	163.16(9)
H-bond length (Å)	O1–H1...O2[d]	2.663(18)	2.718(2)	2.665(3)	2.744(4)

[a] $1/2 - x, -y, -1/2 + z$.
[b] $1/2 - x, 1-y, -1/2 + z$.
[c] $1/2 + x, 1/2 - y, -z$.
[d] $1 - x, 1/2 + y, 1/2 - z$.

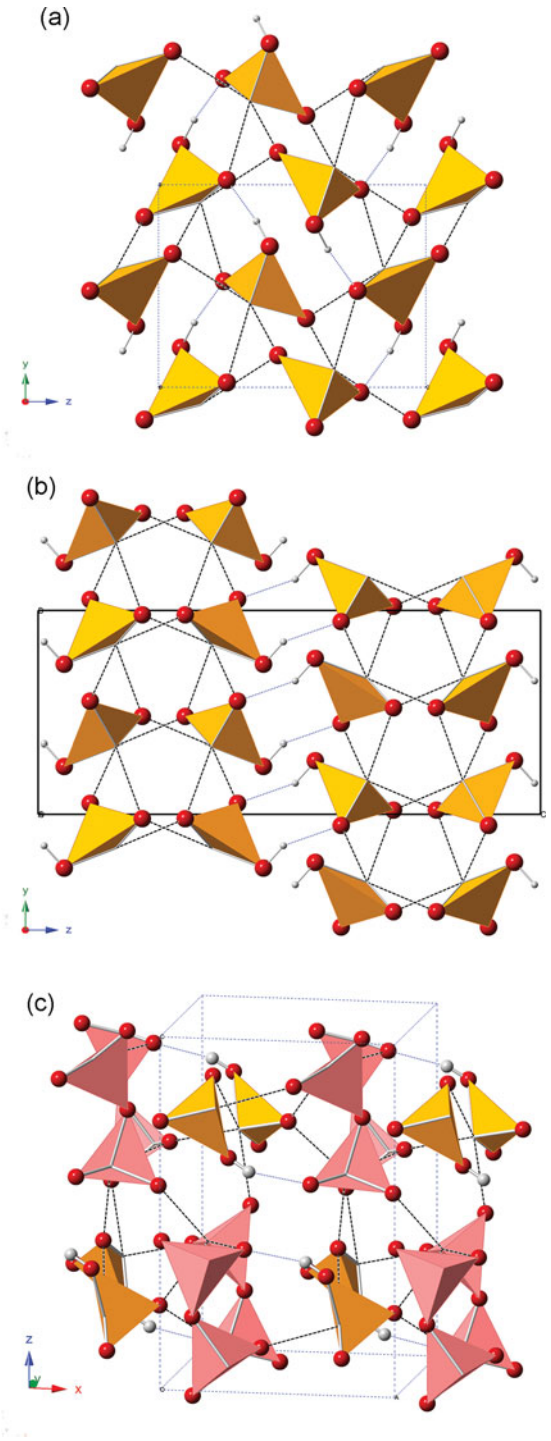

Figure 3. (Colour online) The polyhedral representation of (a) α-HIO_3, (b) γ-HIO_3 (both in *zy* plane), and (c) HI_3O_8 (in *xz*-plane) structures. Blue dotted lines show H…O contacts and dashed black lines show I…O contacts. Red and gray balls represent oxygen and hydrogen atoms, respectively. The pink and yellow pyramids in (c) represent I_2O_5 and HIO_3, respectively.

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