Dimorphism in Mercury(II) Iodate(V): Preparation and Thermal Behaviour of α- and β-Hg(IO$_3$)$_2$, and Single Crystal Structure Analysis of β-Hg(IO$_3$)$_2$

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Mercury(II) iodate(V) is dimorphous and crystallizes in two polymorphs named α- and β-Hg(IO$_3$)$_2$. The α-modification was prepared by precipitation of a slightly acidified Hg(NO$_3$)$_2$ solution with an excess of an aqueous HIO$_3$ solution; for the polycrystalline material unindexed powder data is given. Colourless to light-yellow single crystals of the β-modification, with an edge-length of up to 0.3 mm and a plate-like habit, were grown during hydrothermal treatment (220 °C, 10 d) of the polycrystalline precipitate. The crystal structure of β-Hg(IO$_3$)$_2$ was determined from single crystal X-ray data (space group $P2_1$ (no. 4), $Z = 2$, $a = 5.7818(9)$, $b = 5.6077(10)$, $c = 8.9849(12)$ Å, $\beta = 102.890(2)°$, 1668 structure factors, 83 parameter, $R[F^2 > 2\sigma(F^2)] = 0.0175$, $wR(F^2$ all$) = 0.0382$) and is made up from trigonal pyramidal IO$_3$ groups with an average I-O distance of 1.825 Å and distorted [HgO$_8$] polyhedra with a mean Hg-O bond length of 2.537 Å as the main building units. Infinite zig-zag chains of *cis*-corner-sharing [HgO$_{4/2}$O$_{4/1}$] polyhedra extend parallel to [010]. The chains are connected by IO$_3$ groups along the [100] direction to form layers parallel to the (001) plane. The three-dimensional framework is held together by weak intermolecular I-O interactions > 2.58 Å along the [001] direction. No $\alpha \leftrightarrow \beta$ phase transformation was detected upon heating. Both polymorphs decompose completely in an one-step mechanism around 500 °C.

Key words: Mercury(II), Iodates(V), Dimorphism, Crystal Structure

Introduction

In the past, much attention was drawn to the synthesis and the crystal chemistry of different anhydrous divalent metal salts of iodic acid, M(IO$_3$)$_2$ with $M =$ Ba [1], Ca [2], Cd [3], Co [4], Cu [5, 6], Mg [7], Pb [8], and Zn [9], in particular in view of their potential piezoelectric and electrooptical applications. Frequently, these M(IO$_3$)$_2$ salts are polymorphous and crystallize in polar space groups. For this reason it seemed desirable to grow single crystals and to analyze the crystal structure of the corresponding mercury representative, Hg(IO$_3$)$_2$, whose preparation and chemical properties have been reported nearly 150 years ago [10]. Up to now, numerous phases in the system Hg-I-O(-H) with both mercury and iodine in different oxidation states were compiled [10], or described during systematic investigations on mercury periodates(VII) [11]. Crystallographically well-characterized compounds remain rare and are restricted to only three phases of which structures have been determined from single crystal X-ray data: The mixed-valent mercury(I) mercury(II) oxide iodide Hg$_2$OI [12], and the two mercury(II) periodates(VII) Hg(H$_3$IO$_6$) [13] and Hg$_3$(H$_2$IO$_6$)$_2$ [14].

The results of the preparation and thermal behaviour of two polymorphs, α- and β-Hg(IO$_3$)$_2$, and the crystal structure analysis of the β-modification are reported in this article.

Experimental Section

Polycrystalline α-Hg(IO$_3$)$_2$ was prepared by precipitation of a slightly acidified aqueous Hg(NO$_3$)$_2$ (Merck, p. A.) solution with an excess aqueous HIO$_3$ (Merck, p. A.) solution. The resulting colourless product was filtered off, washed with mother liquor, demineralized water and ethanol and dried in a desiccator over CaCl$_2$ for two days. Single crystals suitable for X-ray analyses of β-Hg(IO$_3$)$_2$ were grown during hydrothermal treatment of the obtained polycrystalline α-polymorph. For that purpose 200 mg of α-Hg(IO$_3$)$_2$ were charged in a Teflon inlay with 10 ml capacity which was two-thirds filled with demineralized water and then sealed in a

Table 1. α-Hg(IO$_3$)$_2$. Calibrated 2θ values (calculated for Cu-K$_{\alpha 1}$ radiation) and relative intensities.

2θ [°]	Relative intensity	2θ [°]	Relative intensity
5.185	16	10.618	11
15.033	40	15.941	10
16.822	6	19.214	26
20.189	7	22.124	114
22.710	19	24.176	11
27.357	1000	30.374	95
31.038	19	32.149	134
32.552	101	33.336	14
34.563	7	35.693	36
36.131	70	37.346	20
38.270	30	39.564	17
40.661	6	42.012	14
44.823	112	45.063	149
46.413	139	47.061	64
49.021	20	49.330	29
50.177	18	52.136	20
53.173	6	54.438	50
55.238	21	56.480	21
57.774	18	58.692	16

steel autoclave. This device was heated up to 220 °C within 3 h, left at that temperature for ten days and cooled down to room temperature in the course of 12 h. After filtering and washing with mother liquor, water and ethanol, light-yellow crystals of β-Hg(IO$_3$)$_2$ with mainly plate-like habit and an edge-length up to 0.3 mm could be isolated. No by-products were detected by subsequent XRPD of the bulk material. Alternatively, single crystals of β-Hg(IO$_3$)$_2$ were grown by boiling the polycrystalline material in diluted nitric acid and subsequent slow evaporation of the remaining filtrate. Crystals prepared by the recrystallization method were poorer in quality compared to the ones obtained by the hydrothermal route.

XRPD measurements of polycrystalline α-Hg(IO$_3$)$_2$ were performed on a Philips X'Pert diffractometer system (Cu-K$_{\alpha 1,2}$ radiation ($\lambda = 1.54060$, 1.54439 Å), Bragg-Brentano geometry, silicon single crystal sample holder, 5 – 70°/ 2θ, 0.02°/ step, 15 s/step). Relative intensities and calibrated d-values using silicon powder as an internal standard are listed for reflections up to 58.69° (2θ) in Table 1.

Single crystal diffraction intensities of β-Hg(IO$_3$)$_2$ were collected in the ω-scan technique with 0.3° rotation width and 30 s exposure time per frame using a SMART three-circle diffractometer (Siemens) equipped with a CCD camera. Three independent sets of 606 frames were measured thus scanning the whole reciprocal sphere. The measured intensities were corrected for Lorentz and polarization effects and an absorption correction was applied using the program HABITUS [15] by minimizing the internal R_i value and optimizing the crystal shape. The so derived habit was the basis of the numerical absorption correction. The crystal structure of β-Hg(IO$_3$)$_2$ was solved by direct methods and re-

Table 2. β-Hg(IO$_3$)$_2$. Crystallographic data and details of data collection, structure solution and refinement.

Diffractometer	Siemens SMART CCD detector
Radiation; wavelength λ [Å]	Mo-K$_\alpha$; 0.71073
Temperature [°C]	22(2)
Crystal dimensions [mm^3]	0.10·0.10·0.04
Crystal description	colourless plate
Space group	$P2_1$ (no. 4)
Formula units	$Z = 2$
Lattice parameters [Å, °]	$a = 5.7818(9)$
	$b = 5.6077(10)$
	$c = 8.9849(12)$
	$\beta = 102.890(2)$
Volume [Å^3]	$V = 283.97(8)$
Formula weight [g·mol^{-1}]	550.39
μ [mm^{-1}]	37.93
X-ray density [g·cm^{-3}]	6.437
Range $\theta_{min} - \theta_{max}$	$2.33 \rightarrow 30.47$
Range $h; k; l$	$-8 \rightarrow 8; -7 \rightarrow 8; -12 \rightarrow 12$
Structure solution and refinement	SHELX97 [16]
Measured reflections	4233
Independent reflections	1668
Observed reflections $[I > 2\sigma(I)]$	1604
R_i	0.0422
Absorption correction	numerical using HABITUS [15]
Transmission coefficients T_{min}/T_{max}	0.0929; 0.4243
Number of parameters	83
Extinction coefficient (SHELXL97)	0.0290(6)
Diff. electron density [e·Å^{-3}] with distance to atom [Å]	$\Delta\rho_{max} = 1.02$ [0.77; Hg] $\Delta\rho_{min} = -0.98$ [1.12; O3]
$R[F^2 > 2\sigma(F^2)]$; $wR(F^2$ all)	0.0175; 0.0382
Goof	1.047
Flack parameter [18]	0.001(5)
CSD-number	413033

Table 3. β-Hg(IO$_3$)$_2$. Atomic coordinates and equivalent isotropic displacement parameters [Å^2].

Atom	Position Wyckoff	x	y	z	U_{eq}[a]
Hg	2a	0.06995(3)	0.75175(4)	0.17305(2)	0.01636(6)
I1	2a	0.27243(5)	0.26425(6)	0.57293(3)	0.01210(8)
I2	2a	0.42326(5)	0.22972(6)	0.14913(3)	0.01134(8)
O1	2a	0.0343(8)	0.0622(8)	0.5872(6)	0.0262(10)
O2	2a	0.1704(7)	0.4231(7)	0.0661(5)	0.0195(8)
O3	2a	0.2411(8)	0.4311(7)	0.7421(5)	0.0185(8)
O4	2a	0.2934(8)	0.0807(7)	0.2937(5)	0.0181(8)
O5	2a	0.3299(7)	0.0023(8)	0.0043(5)	0.0225(9)
O6	2a	0.4744(8)	0.5758(7)	0.3474(5)	0.0211(9)

[a] $U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

fined with the SHELX97 program package [16]. In the final least-squares cycles all atoms were refined anisotropically. The final difference Fourier maps did not indicate any additional atomic sites, and the highest difference peaks were located close to the mercury position. No higher symmetry was suggested by the PLATON program [17], and the

Table 4. β-Hg(IO$_3$)$_2$. Interatomic distances [Å] and angles [°] of the [HgO$_8$] and IO$_3$ polyhedra, as well as bond-valence parameters (BVP) of the corresponding atoms.

Hg	O2	O3[i]	O4[ii]	O2[iii]	O1[i]	O6	O5[ii]	O5[iii]
O2	**2.215(4)**	4.310(6)	4.200(6)	3.480(5)	3.654(7)	2.869(6)	3.455(6)	2.854(6)
O3[i]	142.80(15)	**2.332(4)**	3.149(6)	3.030(6)	2.627(6)	4.500(7)	4.428(6)	3.326(7)
O4[ii]	132.60(15)	84.05(15)	**2.371(4)**	3.815(6)	3.754(6)	3.020(6)	2.691(6)	5.135(6)
O2[iii]	95.56(9)	78.01(15)	103.75(14)	**2.478(4)**	4.660(6)	5.031(7)	2.854(6)	2.637(6)
O1[i]	98.70(15)	64.26(14)	98.25(15)	133.68(14)	**2.591(5)**	3.126(6)	5.238(7)	3.771(6)
O6	70.73(14)	126.90(14)	72.87(14)	153.14(14)	72.50(14)	**2.695(4)**	3.843(7)	5.022(6)
O5[ii]	87.58(15)	121.09(13)	62.92(13)	65.99(13)	157.82(14)	89.85(13)	**2.747(4)**	4.721(7)
O5[iii]	66.99(14)	78.88(15)	157.60(14)	58.65(12)	87.34(14)	129.27(13)	114.57(7)	**2.863(4)**

I1	O1	O6[iv]	O3	I2	O5	O4	O2
O1	**1.810(4)**	2.770(6)	2.627(6)	O5	**1.816(4)**	2.691(6)	2.637(6)
O6[iv]	99.6(2)	**1.818(4)**	2.813(6)	O4	94.8(2)	**1.839(4)**	2.779(6)
O3	92.5(2)	100.98(19)	**1.828(4)**	O2	92.35(19)	98.1(2)	**1.839(4)**

I1...O1[i]	2.621(4)			I2...O3[iv]		2.584(4)	
I1...O4	2.740(4)			I2...O6		2.606(4)	
				I2...O5[v]		2.674(4)	

Symmetry transformations used to generate equivalent atoms: [i] $-x, y+1/2, -z+1$; [ii] $x, y+1, z$; [iii] $-x, y+1/2, -z$; [iv] $-x+1, y-1/2, -z+1$; [v] $-x+1, y+1/2, -z$. **BVP**: Hg 2.03, I1 4.94, I2 4.77, O1 1.88, O2 2.08, O3 1.98, O4 1.90, O5 1.88, O6 1.80
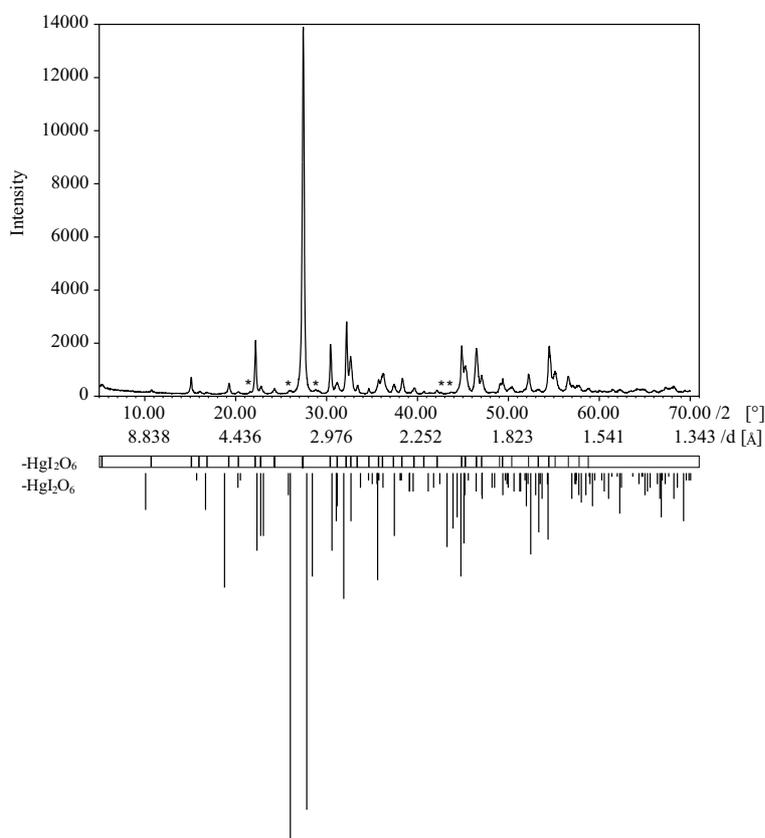

Fig. 1. XRDP pattern of α-Hg(IO$_3$)$_2$ and bar-chart simulation of β-Hg(IO$_3$)$_2$. Reflections of which peak maxima could not be determined reliably are marked with an asterix.

Flack parameter [18] gives a clear indication of the absence of any centre of symmetry. Further details of data collection and structure refinement are summarized in Table 2.

Final atomic coordinates and equivalent isotropic displacement parameters are listed in Table 3, and selected interatomic distances, angles and bond-valence parameters [19]
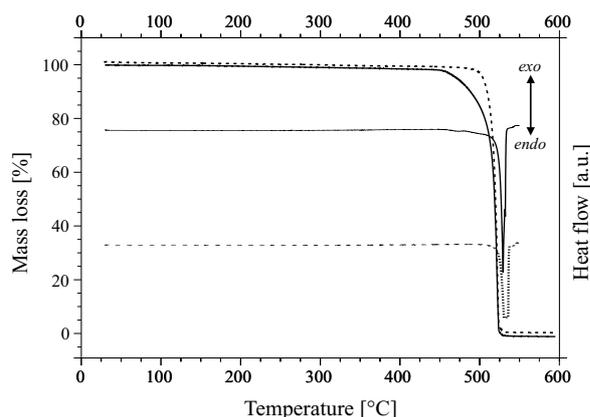
Fig. 2. TG and DSC curves of the thermal decomposition of α- (dotted line) and β-Hg(IO$_3$)$_2$ (solid line).

are given in Table 4. Additional crystallographic information on β-Hg(IO$_3$)$_2$ is available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, email: crysdata@fiz-karlsruhe.de, by quoting the literature citation, the name of the author and the depository number listed at the end of Table 2. Drawing of structural details were produced using the program ATOMS [20].

Thermoanalytical measurements of both polymorphs were performed in an open system under a flowing N$_2$ atmosphere on a Mettler-Toledo TG50 (35 – 600 °C, heating rate 5 °C·min^{-1}, corundum crucibles) and a DSC 25 system (35 – 550 °C, heating rate 5 °C·min^{-1}, aluminium capsules).

Results and Discussion

α-Hg(IO$_3$)$_2$ is formed by fast precipitation of an aqueous mercury(II) nitrate solution with an aqueous iodic acid solution whereas recrystallization from diluted nitric acid or preparation under hydrothermal conditions yields single phase β-Hg(IO$_3$)$_2$. The chemical formula for both phases was confirmed by gravimetric analysis for α-Hg(IO$_3$)$_2$ [21] and on the basis of single crystal structure analysis for β-Hg(IO$_3$)$_2$, respectively. Complementary IR-measurements did not indicate the presence of water for both polymorphs. In Fig. 1 the corresponding diffraction pattern of α-Hg(IO$_3$)$_2$ and the simulation of the β-phase are shown, which indicate that no β-phase is present in the precipitate. However, no reliable indexation of the α-Hg(IO$_3$)$_2$ powder pattern was possible with different indexation programs [22], supposedly caused by the comparatively poor crystallinity and the broad reflections of this phase. During heating, no $\alpha \leftrightarrow \beta$ phase transformation was detected by thermal analysis. Both polymorphs are relatively stable and decompose
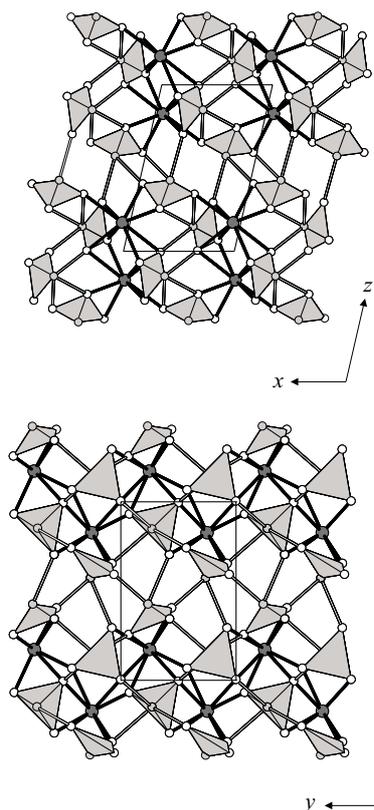

Fig. 3. β-Hg(IO$_3$)$_2$. Projection of the crystal structure along [010] (top) and [100] (bottom); the unit cell is outlined, Hg atoms are given as dark-grey spheres, I atoms as light-grey spheres and O atoms as white spheres. The IO$_3$ anion is plotted in the polyhedral representation and weak I-O bonds are given as open lines.

completely in an one-step mechanism around 500 °C (Fig. 2).

The new structure type of β-Hg(IO$_3$)$_2$ is composed of distorted [HgO$_8$] polyhedra and trigonal IO$_3$ pyramids as the main building units. Infinite zig-zag chains of *cis*-corner-sharing [HgO$_{4/2}$O$_{4/1}$] polyhedra extend parallel to [010]. Adjacent chains are connected by interstitial IO$_3$ groups along the [100] direction. This arrangement leads to a layer-like assembly parallel to (001) which makes the crystal chemical situation of β-Hg(IO$_3$)$_2$ comparable to the layer structures of the iodates(V) Pb(IO$_3$) (polymorph I) [8] and VO$_2$IO$_3$·2H$_2$O [23]. The linkage of the layers takes place only by weak intermolecular O...IO$_3$ interactions along the [001] direction (Fig. 3) which likewise explains the easy cleavage and the plate-like habit of the crystals.

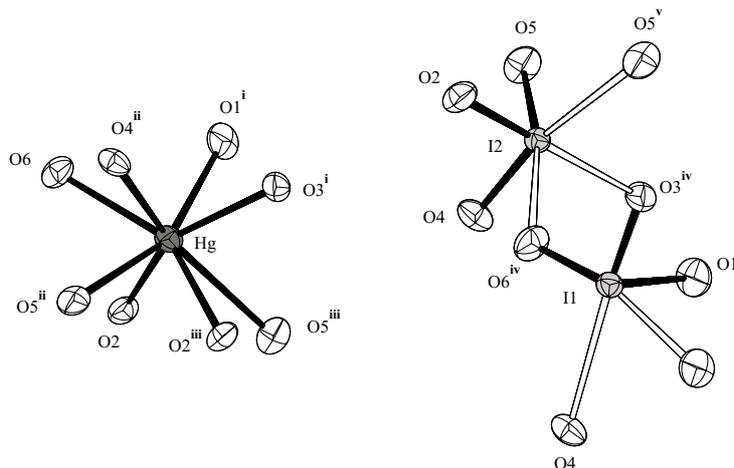Fig. 4. β-Hg(IO$_3$)$_2$. Plot of the [HgO$_8$] polyhedron and the [I$_2$O$_9$] dimer with displacement ellipsoids drawn at the 74% probability level. Short I-O bonds are given as solid lines and weak I-O bonds as open lines; the symmetry codes refer to Table 4.

Unlike in most other [Hg^{II}O$_x$] polyhedra, for which frequently a pronounced linear $[2 + x]$ or $[x + 2]$ coordination by oxygen is observed, the mercury atom in β-Hg(IO$_3$)$_2$ shows no explicit linear arrangement. The resulting coordination figure around the eightfold coordinate mercury atom might be described as an intermediate between a square antiprism and a triangulated dodecahedron (Fig. 4, left). The Hg-O distances range from 2.215(4) – 2.863(4) Å, showing an average of d(Hg-O) = 2.537 Å which is in good agreement with other mercury(II) oxocompounds.

Both iodate(V) anions are distorted and deviate significantly from the C_{3v} symmetry of an ideal trigonal pyramid. The mean distances and angles of $\bar{d}$(I1-O) = 1.819 Å, 97.69° and $\bar{d}$(I2-O) = 1.831 Å,

95.08° are in the typical range for an I^{V}O$_3$ group and are in good agreement with the values observed for the other iodates(V) mentioned above. More remote oxygen atoms at comparatively short intermolecular distances between 2.584(4) and 2.740(4) Å augment the coordination of the iodine atoms and stabilize the crystal structure. The resulting [I1O$_5$] (distorted trigonal bipyramid) and [I2O$_6$] (distorted octahedron) polyhedra build [I$_2$O$_9$] dimeric units by edge-sharing (Fig. 4, right).

Under the consideration that weak I-O interactions between 2.584(4) and 2.740(4) Å are not negligible, the oxygen atoms show coordination numbers of {2+1} for O1, O3, O4 and O6, {3} for O2 and {3+1} for O5.

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