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, $\beta = 102.890(2)^\circ$, 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