

# Synthesis and Crystal Structure of $\text{Hg}_2\text{V}_8\text{O}_{20}$ – the First Ternary Mercury Vanadate with Mixed-valent Vanadium (IV/V)

Matthias Weil<sup>a</sup>, Berthold Stöger<sup>a</sup>, Annemarie L. Wessels<sup>b</sup>, and Wolfgang Jeitschko<sup>b</sup>

<sup>a</sup> Institute for Chemical Technologies and Analytics – Division of Structural Chemistry,  
Vienna University of Technology, Getreidemarkt 9/164-SC, A-1060 Vienna, Austria

<sup>b</sup> Institut für Anorganische und Analytische Chemie, Universität Münster,  
Corrensstraße 36, D-48149 Münster, Germany

Reprint requests to PD Dr. M. Weil. E-mail: mweil@mail.zserv.tuwien.ac.at

*Z. Naturforsch.* **2007**, 62b, 1390–1396; received May 29, 2007

Black needle-shaped single crystals of  $\text{Hg}_2\text{V}_8\text{O}_{20}$  were obtained by heating amorphous precipitates resulting from mixing aqueous solutions of  $\text{HgNO}_3\text{OH}$  and  $\text{NH}_4\text{VO}_3$  (Hg : V ratios between 1 : 2.0 and 1 : 2.5) in evacuated silica ampoules at 450 °C for two weeks. Their crystal structure was determined from single crystal diffractometer data [ $C2/m$ ,  $Z = 2$ ,  $a = 22.375(1)$ ,  $b = 3.6312(2)$ ,  $c = 9.6113(4)$  Å,  $\beta = 91.708(5)^\circ$ ,  $R[F^2 \geq 2\sigma(F^2)] = 0.0681$ , 807  $F^2$  values, 61 variable parameters]. Two of the four independent vanadium atoms are surrounded by six close oxygen atoms whereas the other two have five oxygen neighbors. These coordination polyhedra share edges and corners resulting in puckered layers with an overall composition  $[\text{V}_4\text{O}_{10}]^-$  extending parallel to (100). The layers are linked by  $\text{Hg}_2^{2+}$  dumbbells ( $d(\text{Hg}-\text{Hg}) = 2.510(2)$  Å) with a short Hg–O distance of 2.13(2) Å ( $\angle(\text{O}9-\text{Hg}-\text{Hg}) = 173.8(5)^\circ$ ). Although  $\text{Hg}_2\text{V}_8\text{O}_{20}$  crystallizes in a new structure type, it resembles the structures of other layered vanadium oxides with open frameworks and can be classified as being of the Q-UD-type. The near-neighbor environments of the four vanadium positions of this reduced vanadate with an average oxidation number of +4.75 of the vanadium atoms are similar with respect to V–V bonding and it is suggested that the vanadium atoms have delocalized V–V bonding with intermediate valence.

**Key words:** Mercury, Vanadium, Crystal Structure, Mixed Valence, Vanadium Oxide Framework