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)

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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 HgNO_3OH and NH_4VO_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 $[\text{V}_4\text{O}_{10}]^{2-}$ extending parallel to (100). The layers are linked by Hg_2^{2+} dumbbells ($d(\text{Hg}-\text{Hg}) = 2.510(2)$ Å) with a short Hg–O distance of 2.13(2) Å ($\angle(\text{O9}-\text{Hg}-\text{Hg}) = 173.8(5)^\circ$). 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

Introduction

Numerous mercury vanadates with different oxidation states of mercury have been listed in one of the older handbooks on vanadium and its compounds [1]. In the meantime, some of these phases have been structurally characterized, including the high-temperature modification (β -phase) of $\text{Hg}^{\text{II}}\text{V}^{\text{V}}_2\text{O}_6$ [2], the structure of which has later been re-determined [3], the dimorphic compound $\text{Hg}^{\text{II}}_2\text{V}^{\text{V}}_2\text{O}_7$ with its low- [4] and high-temperature [5] modifications, both resembling the pyrochlore structure, and the mercury vanadates with the empirical formulas HgVO_3 and Hg_2VO_4 [6]. HgVO_3 contains mercury in oxidation state +1 and may be expressed as $(\text{Hg}^{\text{I}}_2)(\text{V}^{\text{V}}\text{O}_3)_2$, whereas Hg_2VO_4 contains mixed valent mercury in oxidation states +1 and +2 and can be regarded as a basic mercury(II) adduct of HgVO_3 , leading to the formula $(\text{Hg}^{\text{I}}_2)(\text{V}^{\text{V}}\text{O}_3)_2 \cdot 2\text{Hg}^{\text{II}}\text{O}$. With the possible exceptions of the ternary phases with the tentative com-

positions $\text{Hg}_x\text{V}_2\text{O}_5$ ($0.16 \leq x \leq 0.20$), $\text{Hg}_4\text{V}_{18}\text{O}_{39}$, α - and β - HgV_2O_4 , and HgV_2O_5 , which were obtained as microcrystalline products in the system $\text{HgO}-\text{V}_2\text{O}_3-\text{V}_2\text{O}_5$ at high-pressure conditions (2.5 to 7.7 GPa) [7], all reported ternary mercury vanadates [1, 8] comprise vanadium in oxidation state +5. However, lower oxidation states for vanadium were also observed for quaternary mixed metal/non-metal framework structures in the system $\text{Hg}-\text{V}-\text{P}-\text{O}-(\text{H})$ where the crystal structures have recently been determined for the orthophosphates $(\text{Hg}_2)_2\text{VO}(\text{PO}_4)_2$ [9] and $\text{Hg}_{4-x}\text{O}_{1-y}(\text{VO})(\text{PO}_4)_2 \cdot (\text{H}_2\text{O})$ [10] with vanadium in oxidation state +4 and the diphosphate $\text{HgV}_2(\text{P}_2\text{O}_7)_2$ [11] with vanadium in oxidation state +3.

In the present communication we report the first ternary mercury vanadate with mixed-valent vanadium(IV/V). It has the composition $\text{Hg}_2\text{V}_8\text{O}_{20}$ and was obtained during phase formation studies of the system $\text{Hg}-\text{V}-\text{O}$.

Table 1. Details of selected batches for thermal treatment of precipitated mercury vanadates.

Batch for precipitation experiment			Color and approximate composition of the precipitate	Batch for ampoule experiment	Resulting products
I	HgNO_3OH NH_4VO_3	1.207 g 1.026 g	dark-orange; HgV_2O_6	0.297 g precipitate	elemental mercury; $\text{Hg}_2\text{V}_8\text{O}_{20}$ as tiny black needles
II	HgNO_3OH NH_4VO_3 , NH_4^+ -free	1.195 g 1.031 g	light-brown; $\text{Hg}_2\text{V}_6\text{O}_{17}$	0.318 g precipitate	orange microcrystalline β - HgV_2O_6 and HgO
III	HgNO_3OH NH_4VO_3 , NH_4^+ -free	1.206 g 1.254 g	light-brown; $\text{Hg}_2\text{V}_6\text{O}_{17}$	0.299 g precipitate 0.332 g HgO	orange microcrystalline β - HgV_2O_6 ; few single crystals of HgVO_3 and Hg_2VO_4
IV	HgNO_3OH NH_4VO_3 , NH_4^+ -free	1.201 g 1.025 g	light-brown; $\text{Hg}_2\text{V}_6\text{O}_{17}$	0.309 g precipitate 1.302 g HgO	orange microcrystalline $\text{Hg}_6\text{V}_2\text{O}_{11}$ [8] and HgO ; few single crystals of HgO .
V	HgNO_3OH NH_4VO_3	1.209 g 1.252 g	dark-orange; $\text{Hg}_2\text{V}_6\text{O}_{17}$	0.305 g precipitate 1.95 g HgO	orange microcrystalline β - HgV_2O_6 ; orange block-like crystals of HgO ; unknown microcrystalline phase(s).

Experimental Section

Preparation

Precipitation reactions. For precipitation of mercuric vanadates from aqueous solutions, “ $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ” (Fluka, 99 %; note that the commercially available product “ $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ” is in fact HgNO_3OH) was dissolved in 30 mL of diluted nitric acid ($\text{pH} \approx 3$) and under continuous stirring was added to vanadate(V) solutions (the molar ratios $\text{Hg} : \text{V}$ varied between 1 : 2.0 and 1 : 2.5). The vanadate(V) solutions were prepared by dissolution of NH_4VO_3 (Merck, p. A.) in 20 mL of a 5 wt-% KOH solution to which 2N HNO_3 was slowly added until a color change from yellow to orange was observed ($\text{pH} \approx 7-8$). This solution was separated into two parts. One part was repeatedly heated to dryness and re-dissolved in a diluted KOH solution to remove ammonium (“ NH_4^+ -free vanadate(V)”), the other part remained unchanged (“ NH_4^+ -containing vanadate(V)”).

For all batches “ $\text{Hg}^{2+} + \text{NH}_4^+$ -free vanadate(V) solutions” and “ $\text{Hg}^{2+} + \text{NH}_4^+$ -containing vanadate(V) solutions” yellow to orange solids precipitated which darkened to an orange to brown color after boiling the suspensions for 30 min. The solids were filtered off, washed with mother liquor, water and isopropanol and dried under vacuum in a desiccator overnight. Energy-dispersive X-ray fluorescence spectra of these precipitates revealed vanadium contents between 60 and 80 at-%. The X-ray powder pattern of the solids obtained from the batches “ $\text{Hg}^{2+} + \text{NH}_4^+$ -containing vanadate(V) solutions” showed only very few diffuse reflections which could not be assigned to any known phase. For batches “ $\text{Hg}^{2+} + \text{NH}_4^+$ -free vanadate(V) solutions” a well-crystallized material was obtained. Its energy-dispersive X-ray fluorescence spectrum revealed a phase with 70–80 at-% of vanadium, leading to a tentative composition $\text{Hg}_2\text{V}_6\text{O}_{17}$. Indexing of Guinier data with the program VISSER [12] gave a C-centered monoclinic cell with

dimensions of $a = 7.293(1)$, $b = 9.036(1)$, $c = 5.006(1)$ Å, $\beta = 104.09(1)^\circ$, but it was not possible to grow larger crystals of this compound or to solve the structure from powder data.

Thermal treatment of precipitated mercury vanadates: For thermal treatment, the dried precipitation products or mixtures of the precipitates and of HgO were heated in sealed and evacuated silica glass ampoules. The ampoules had volumes between 5 and 10 mL and were annealed between 400 and 450 °C for 11 to 14 days. The products were rinsed out with acetone and were inspected under a polarizing microscope. Selected crystals and the bulk products were studied by single crystal and X-ray powder diffraction, respectively. Details of selected batches for single crystal growth are given in Table 1.

X-Ray fluorescence analysis and X-ray diffraction

Semi-quantitative analyses of the compounds were carried out in a scanning electron microscope (Leica, type 420i) with an EDAX (energy-dispersive analysis of X-rays) attachment. Only elements with an atomic number higher than Na could reliably be detected. Microcrystalline samples were characterized by X-ray powder diffraction (XRPD). For that purpose an Enraf-Nonius FR 552V Guinier camera ($\text{CuK}\alpha_1$ radiation, α -quartz ($a = 4.9130$, $c = 5.4046$ Å) as internal standard) and a Philips X'Pert Pro diffractometer (Bragg-Brentano geometry, $\text{CuK}\alpha_{1,2}$ radiation, single crystal silicon sample holder, linear PSD detector, step width 0.02° , acquisition time 8 s step^{-1}) were used.

The tiny black needles (Fig. 1) of the title compound were obtained only after thermal treatment of precipitates from “ $\text{Hg}^{2+} + \text{NH}_4^+$ -containing vanadate(V) solutions” and without addition of HgO (Table 1, batch I). They had a maximal length of up to 3 mm and their EDAX measurements showed a $\text{Hg} : \text{V}$ ratio between 1 : 3 and 1 : 4. When the flexible black needles were cut to a length suitable for X-ray measurement, this resulted frequently in fraying of the crystals.

Table 2. Details of data collection, structure solution and refinement for $\text{Hg}_2\text{V}_8\text{O}_{20}$.

Formula weight, g mol^{-1}	1128.70
Space group	$C2/m$, No. 12
Crystal dimensions, mm^3	$0.500 \times 0.001 \times 0.001$
Crystal description	black tiny needle
Formula units Z	2
Lattice parameters	Guinier data,
	<i>Single crystal data</i>
a , Å	22.375(1), 22.345(9)
b , Å	3.6312(2), 3.6279(14)
c , Å	9.6113(4), 9.592(4)
β , deg	91.708(5), 91.725(8)
Volume, Å ³	780.55(6), 777.2(5)
μ , mm^{-1}	24.25
D_x (calcd), g cm^{-3}	4.802
Range $\theta_{\min} - \theta_{\max}$, deg	2.76–24.99
hkl range	$-26 \leq h \leq 26$; $-4 \leq k \leq 4$; $-11 \leq l \leq 11$
Measured reflections	3475
Independent reflections	807
Observed reflections $I \geq 2\sigma(I)$	641
R_{int}	0.0822
Transmission $T_{\min}/T_{\max}$	0.029/0.976
Number of ref. parameters	61
Goof	1.038
$R[F^2 \geq 2\sigma(F^2)]/wR(F^2 \text{ all})$	0.0681/0.1889
$\Delta\rho_{\text{fin}}$ (max/min), e Å^{-3}	7.91 (0.94, Hg)/–4.40; 1.00, Hg)
(dist. to atom, Å)

Fig. 1. The typical needle-like habit of the $\text{Hg}_2\text{V}_8\text{O}_{20}$ crystals, shown here on a scanning electron microscope photograph.

However, it was possible to separate a very tiny needle and to pin it along the needle axis on a glass fiber. The crystal was then measured on a Bruker Smart-Apex CCD diffractometer in the ω and φ scan technique with 0.3° rotation width and 60 s exposure time per frame. Three independent sets of 600 frames were recorded, thus scanning the entire reciprocal sphere up to $\theta = 28^\circ$ with high redundancy. Because the crys-

Table 3. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for $\text{Hg}_2\text{V}_8\text{O}_{20}$. All atoms are located on mirror planes (Wyckoff position $4i, x0z$).

Atom	x	z	U_{eq}^a
Hg	0.48156(5)	0.37538(11)	0.0218(5)
V1	0.11987(19)	0.1988(4)	0.0105(10)
V2	0.18807(19)	0.5346(4)	0.0108(10)
V3	0.25710(19)	0.2304(5)	0.0106(10)
V4	0.39853(19)	0.0582(4)	0.0091(10)
O1	0.0602(8)	0.286(2)	0.021(5)
O2	0.0962(8)	0.003(2)	0.021(5)
O3	0.1191(8)	0.5744(19)	0.018(4)
O4	0.1795(7)	0.3327(19)	0.013(4)
O5	0.2201(8)	0.0865(19)	0.015(4)
O6	0.2292(7)	0.7206(18)	0.012(4)
O7	0.2884(7)	0.4580(19)	0.014(4)
O8	0.3406(8)	0.1632(19)	0.014(4)
O9	0.4602(9)	0.158(2)	0.024(5)
O10	0.6248(7)	0.1438(18)	0.011(4)

$$^a U_{\text{eq}} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* \cdot a_j^* a_i \cdot a_j.$$

Table 4. Interatomic distances (Å) and angles ($^\circ$). Only distances shorter than 3.5 Å are listed.

Hg–O9	2.13(2)	V3–O5	1.590(19)
Hg–Hg	2.510(2)	V3–O6	1.898(5)
Hg–O1	2.688(13)	V3–O8	1.996(18)
Hg–O3	2.944(13)	V3–O4	2.021(17)
V1–O1	1.597(19)	V3–O7	2.276(18)
V1–O4	1.826(18)	V3–V1	3.076(6)
V1–O10	1.895(5)	V3–V2	3.120(5)
V1–O2	1.94(2)	V3–V2	3.347(6)
V1–O5	2.518(18)	V4–O9	1.66(2)
V1–V3	3.076(6)	V4–O8	1.665(18)
V1–V4	3.084(5)	V4–O2	1.913(6)
V2–O3	1.600(17)	V4–O10	1.996(18)
V2–O7	1.891(5)	V4–O5	3.473(15)
V2–O4	1.944(19)	V4–V1	3.084(5)
V2–O6	1.986(18)		
V2–O7	2.383(17)		
V2–V3	3.120(5)	O9–Hg–Hg	173.8(5)
V2–V3	3.347(6)		
V2–V2	3.395(7)		

tal diffracted very weakly, nearly no intensity was observed for the high angles reflections and thus the data set was cut off for reflections with $\theta > 25.0^\circ$. An absorption correction was applied using the multi-scan approach with the program SADABS [13]. The structure determination revealed the formula $\text{Hg}_2\text{V}_8\text{O}_{20}$. The crystal structure was solved by Direct Methods and refined with the SHELXTL program package [14] in space group $C2/m$. The positions of mercury and of some vanadium atoms could be determined directly and all other atoms were subsequently found from difference Fourier syntheses. In the final refinement cycles the positions of the metal atoms were refined with anisotropic and those of the oxygen atoms with isotropic displacement parameters. The final difference Fourier maps did not indicate any additional atomic sites, and the highest difference peaks were located

very close to the mercury positions (Table 2). Because lattice parameters from single crystal data are usually affected by systematic errors due to absorption, we calculated the interatomic distances with the lattice parameters from Guinier powder data. However, a comparison of the interatomic distances using both Guinier and single-crystal data reveals that they are the same within the standard deviations. Further details of the data collection and the crystal data are summarized in Table 2. Atomic parameters and selected interatomic distances and angles are listed in Tables 3 and 4. Drawings of structural details were produced using the program ATOMS [15].

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-418029.

Results and Discussion

It is obvious that $\text{Hg}_2\text{V}_8\text{O}_{20}$ was solely obtained after thermal treatment of precipitates with an approximate composition of HgV_2O_6 that were prepared from batches “ $\text{Hg}^{2+} + \text{NH}_4^+$ -containing vanadate(V) solutions”, whereas treatment of precipitates obtained from NH_4^+ -free solutions led to other products (Table 1). This points to the presence of minor amounts of ammonium cations in the precipitates of the untreated vanadate(V) solutions. When the samples are annealed in closed silica ampoules, NH_3 with its slightly reducing properties is then released which subsequently leads to the reduction of a part of vanadium(V) to vanadium(IV) [16] and of Hg(II) to Hg(I) and Hg(0) , resulting in formation of $\text{Hg}_2\text{V}_8\text{O}_{20}$. This is supported by the observation that a gas (apparently N_2) was released when the ampoules were opened (caution!). Such complex interplays between different redox equilibria of different mercury and other species have likewise been observed for various systems in closed ampoules or under hydrothermal conditions, *viz.* for Hg-P-O [17], Hg-As-O [18], Hg-V-O [6], Hg-Cr-O [19], and Hg-Mo-O [20]. As proof that no nitrogen (as N^{3-}) was incorporated into the structure of $\text{Hg}_2\text{V}_8\text{O}_{20}$, we carried out “direct syntheses” from vanadium oxides and mercury metal and/or mercury oxide under similar conditions as described in the Experimental Section (closed silica ampoules, 450 °C, 10 d). The idealized redox-reactions are given in Eq. 1–3.

Fig. 2. The crystal structure of $\text{Hg}_2\text{V}_8\text{O}_{20}$ in the polyhedral representation projected along [010] (a) and along [001] (b), emphasizing the layered character. Hg atoms are given as dark-grey spheres, O atoms as small black-rimmed spheres; strong Hg–O bonds are indicated as solid lines, weak Hg–O bonds as dotted lines. The quadruple chains of edge-sharing VO_6 octahedra (Q) are given as light-grey polyhedra and the UD chains of the (idealized) square pyramids are displayed in dark-grey.

In each case orange to dark-brown microcrystalline products were obtained with $\text{Hg}_2\text{V}_8\text{O}_{20}$ as the main

Fig. 3. Details of the $[\text{V}_4\text{O}_{10}]^{4-}$ layer with the atom numbering scheme. V atoms are represented as ellipsoids at the 75 % probability level and O atoms as spheres with arbitrary radii. The weak V1–O5 bond is indicated with dotted lines.

phase, as revealed by X-ray powder diffraction measurements. Besides minor amounts of unreacted mercury (clearly visible as mercury droplets), V_2O_5 and HgVO_3 [6] were identified during the phase analyses. Only for the reaction according to Eq. 3, one reflection at $2\theta = 24.56^\circ$ could not be assigned to any known phase of the system Hg – V – O .

$\text{Hg}_2\text{V}_8\text{O}_{20}$ crystallizes in a new structure type and exhibits the highest vanadium content of a mercury vanadate structurally characterized so far. The asymmetric unit contains one mercury, four vanadium and ten oxygen atoms. The building blocks of the crystal structure are puckered polyvanadate layers with an overall composition of $[\text{V}_4\text{O}_{10}]^{4-}$ extending parallel to (100) which are linked *via* pairs of mercury(I) atoms (Fig. 2).

The mercury atoms are symmetry-related by an inversion center leading to a Hg_2^{2+} dumbbell with a symmetric oxygen environment. The $\text{Hg}^{\text{I}}\text{--Hg}^{\text{I}}$ distance of 2.510(2) Å is typical for such a dumbbell and is in very good agreement with the average distance of 2.518(25) Å calculated for more than 100 independent Hg_2^{2+} groups observed for various inorganic mercurous oxo-compounds [21]. Another characteristic feature of this structure family is the formation of linear or nearly linear single building units $[\text{O--Hg--Hg--O}]$ with two O atoms tightly bonded to the dumbbell. The bond angle Hg--Hg--O of $173.8(5)^\circ$ deviates only slightly from 180° and the corresponding Hg--O distance of 2.13(2) Å is comparable with the average $\text{Hg}(\text{I})\text{--O}$ distance of 2.17 Å found in more than 30 mercurous oxo-compounds [22]. The coordination sphere of the mercury atom is augmented by four re-

mote O atoms of the vanadate layers at distances of 2.688(13) ($2\times$) and 2.944(13) Å ($2\times$), which leads to an additional cohesion between the dumbbells and the vanadate layers.

Following one of the latest reviews on multinary vanadium oxides with open framework structures [23], the upper limit for a V–O distance to be considered as bonding is 2.6 Å. Then three of the four vanadium atoms (V1–V3) have six oxygen neighbors whereas the vanadium atom V4 has five oxygen neighbors, leading to distorted octahedra with one short V=O bond and a distorted trigonal bipyramid with two V=O bonds as corresponding coordination polyhedra. However, for a better classification of the $[\text{V}_4\text{O}_{10}]^{4-}$ layer considering the structural chemistry of vanadium oxide frameworks as derived in [23], we will hereafter describe the vanadium coordination polyhedra only for V–O distances < 2.5 Å. Then the oxygen environment for V1 becomes also trigonal-bipyramidal. If we further ignore the differences between a distorted trigonal bipyramid (TB) and a square pyramid (SP), the vanadium oxide framework of the $[\text{V}_4\text{O}_{10}]^{4-}$ layer can be regarded as being of the Q-UD type of structures [23], where Q is a quadruple chain of edge-sharing VO_6 octahedra and UD are square pyramids that share only two neighboring edges with their apices directed up (U) and down (D) (Fig. 2).

As is known for all polyvanadates or multinary vanadium oxides with open frameworks, the V–O bond lengths within the $[\text{V}_4\text{O}_{10}]^{4-}$ layer vary considerably, depending on the coordination number (CN) of the vanadium atoms and the function of the oxygen atoms as terminal or bridging (Table 4, Fig. 3). The five V–O

distances to the terminal oxygen atoms O1, O3, O5, O8, and O9 are the shortest, with an average of 1.60 Å for the three vanadium atoms V1–V3, and the two V–O distances of 1.66 Å for the vanadium atom V4. Aiming for simplicity, these short V–O bonds are sometimes considered as double bonds within the vanadyl group “–V=O” [23], as we have done above. The V4–O8 and V4–O9 bonds of 1.66 Å are longer than the V–O bonds of ~ 1.60 Å to the other terminal oxygen atoms because the V4 atom has two such terminal oxygen neighbors as compared to the one for the other vanadium atoms.

Of the ten different oxygen atoms the O9 atom is strongly bonding to the mercury dumbbell as the second coordination partner, whereas the other terminal oxygen atoms show only weak (O1, O3) or no interactions with the mercury atoms. The bridging oxygen atoms within the polyanion have two (O8), three (O2, O4, O6, O10), or four vanadium (O7) neighbors, respectively. Thus, their individual V–O bonds are generally weaker and the average V–O distances consequently are longer, with 1.831 Å for the two-fold, 1.927 Å for the three-fold, and 2.110 Å for the four-fold coordinated O atoms, respectively.

Finally, we consider the vanadium-vanadium interactions. With 40 negative formal charges at the 20 oxygen atoms and 2 positive charges at the mercury atoms there remain 38 positive charges to be distributed among the 8 vanadium atoms of the formula $\text{Hg}_2\text{V}_8\text{O}_{20}$. Thus, there are two electrons per formula unit which are located within the vanadium-oxygen polyanion and which do not participate in vanadium-oxygen bonding. Since there are four vanadium positions, all with equal multiplicity in the compound, one is tempted to look at the interatomic distances to see whether there is one with greater average V–O bond length. The corresponding V atom could then be assigned the oxidation number +4. Because, depend-

ing on the CN, the average $\text{V}^{\text{IV}}\text{–O}$ distances should be between 0.04 and 0.07 Å longer than the average $\text{V}^{\text{V}}\text{–O}$ distances [24]. This is, however, not the case. In $\text{Hg}_2\text{V}_8\text{O}_{20}$ there is no single atom whose average V–O distance is that much larger than all of the others, irrespective on how we define the CN of the V1 atom. We may ignore the rather large V1–O5 distance of 2.518 Å. Then V1 obtains a CN of 5 like the V4 atom, but their average bond lengths are the same with 1.831 and 1.829 Å, respectively. We may count the V1–O5 distance of 2.518 Å as bonding. The V1 atom may then be considered to have 6 oxygen neighbors like the V2 and the V3 atoms, but again, the average V–O bond lengths of these vanadium atoms are practically the same with 1.945, 1.949, and 1.947 Å, respectively. Thus, there is no single vanadium position which could be regarded as that of a vanadium atom of oxidation state +4. This is also supported by considering the V–V distances. The four different vanadium atoms all have at least two V neighbors at distances shorter than 3.13 Å, but they have none at a distance of say 2.8 or 2.9 Å, which may be considered typical for a localized V–V bond in semiconducting reduced binary vanadium oxides ([25, 26] and references therein). In contrast, the shortest V–V bonds in $\text{Hg}_2\text{V}_8\text{O}_{20}$ are all in between 3.07 and 3.13 Å and compare rather well with the bonding V–V interactions of the high-temperature modifications of these reduced oxides with metallic conductivity. Thus, we conclude that the four different vanadium positions in $\text{Hg}_2\text{V}_8\text{O}_{20}$ all have similar bonding characteristics with intermediate valences.

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- [1] *Gmelins Handbuch der Anorganischen Chemie 48: Vanadium B2*, 8th ed. Verlag Chemie, Weinheim, **1967**, pp. 542–543.
 - [2] J. Angenault, A. Rimsky, *C. R. Acad. Sci. Série C* **1968**, 266, 978–980.
 - [3] T. J. Mormann, W. Jeitschko, *Z. Kristallogr. NCS* **2000**, 216, 3–4.
 - [4] M. Quarton, J. Angenault, A. Rimsky, *Acta Crystallogr.* **1973**, B29, 567–573.
 - [5] A. W. Sleight, *Mater. Res. Bull.* **1972**, 7, 827–830.
 - [6] A. L. Wessels, W. Jeitschko, *J. Solid State Chem.* **1996**, 125, 140–146.
 - [7] V. L. Volkov, B. G. Golovkin, A. S. Fedyukov, Yu. G. Zainulin, *Russ. J. Inorg. Chem.* **1990**, 35, 1660–1663.
 - [8] J. Angenault, *Rev. Chim. Minér.* **1970**, 7, 651–699.
 - [9] E. le Fur, J. Y. Pivan, *J. Solid State Chem.* **2001**, 158, 94–99.
 - [10] E. le Fur, R. Gautier, E. Furet, J. Y. Pivan, *Inorg. Chem.* **2002**, 41, 4227–4231.

- [11] S. Boudin, A. Grandin, A. Leclaire, M.M. Borel, B. Raveau, *J. Mater. Chem.* **1994**, *4*, 1889–1892.
- [12] J. W. Visser, *J. Appl. Crystallogr.* **1969**, *2*, 89–95.
- [13] G. M. Sheldrick, SADABS (version 2.01), Bruker AXS Inc., Madison, Wisconsin (USA) **1997**.
- [14] G. M. Sheldrick, SHELXTL (version 5.10), Bruker AXS Inc., Madison, Wisconsin (USA) **1997**.
- [15] E. Dowty, ATOMS for Windows (version 6.3), Shape Software, Kingsport, TN (USA) **2006**.
- [16] K. J. Range, R. Zintl, A. M. Heyns, *Z. Naturforsch.* **1988**, *43b*, 309–317.
- [17] M. Weil, R. Glaum, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1752–1761; M. Weil, R. Glaum, *J. Solid State Chem.* **2001**, *157*, 68–75.
- [18] A. L. Wessels, W. Jeitschko, M. H. Möller, *Z. Naturforsch.* **1997**, *52b*, 469–473; M. Weil, *Z. Anorg. Allg. Chem.* **2004**, *630*, 213–214; M. Weil, *Z. Naturforsch.* **2000**, *55b*, 699–706.
- [19] A. L. Wessels, R. Czekalla, W. Jeitschko, *Mater. Res. Bull.* **1998**, *33*, 95–101; B. Stöger, M. Weil, *Z. Naturforsch.* **2006**, *61b*, 708–714; M. Weil, B. Stöger, *J. Solid State Chem.* **2006**, *179*, 2479–2486; M. Weil, B. Stöger, E. Zobetz, E. J. Baran, *Monatsh. Chem.* **2006**, *137*, 987–996; M. Weil, B. Stöger, *Acta Crystallogr.* **2006**, *E62*, i199–i200.
- [20] T. J. Mormann, W. Jeitschko, *Z. Anorg. Allg. Chem.* **2001**, *627*, 224–233; A. L. Wessels, W. Jeitschko, *Z. Naturforsch.* **1996**, *51b*, 37–41; A. L. Wessels, W. Jeitschko, *J. Solid State Chem.* **1997**, *128*, 205–208; T. J. Mormann, W. Jeitschko, *Inorg. Chem.* **2000**, *39*, 4219–4223.
- [21] M. Weil, E. Tillmanns, D. Yu. Pushcharovsky, *Inorg. Chem.* **2005**, *44*, 1443–1451.
- [22] A. L. Wessels, Dissertation. Westfälische Wilhelms-Universität, Münster (Germany) **1996**.
- [23] P. Y. Zavilij, M. S. Whittingham, *Acta Crystallogr.* **1999**, *B55*, 627–663.
- [24] R. D. Shannon, *Acta Crystallogr.* **1976**, *A32*, 751–767.
- [25] J. B. Goodenough, *J. Solid State Chem.* **1971**, *3*, 490–500.
- [26] Y. Oka, Sh. Sato, T. Yao, N. Yamamoto, *J. Solid State Chem.* **1998**, *141*, 594–598.