

## Location of Hydrogen Atoms in Tetragonal and Monoclinic Modifications of $\beta_1$ -V<sub>2</sub>H

LINUS PAULING

*Linus Pauling Institute of Science and Medicine, 440 Page Mill Road,  
Palo Alto, California 94306*

Received December 7, 1987; in revised form November 7, 1988

On the basis of knowledge about atomic sizes and the dependence of bond length on bond number, positions are assigned to the hydrogen atoms in tetragonal and monoclinic  $\beta_1$ -V<sub>2</sub>H. The structures may be described as containing linear VHV complexes, with V-H half-bonds, length about 1.76 Å, and the arrangements of these complexes determine the crystal parameters. © 1989 Academic Press, Inc.

The tetragonal form of  $\beta_1$ -V<sub>2</sub>H was made by Voda *et al.* (1) by stretching a tensile-strength bar of the compound. It has  $a = 6.0012$  Å,  $c = 6.6188$  Å,  $Z = 8$ , and volume 29.80 Å<sup>3</sup> per V<sub>2</sub>H. The unstretched compound, also studied by Voda *et al.* and then by Marsh (2), who revised the space-group determination and evaluated the parameters more accurately, has  $a = 4.4566$  Å,  $b = 3.0022$  Å,  $c = 4.4760$  Å,  $\beta = 95.609^\circ$ ,  $Z = 2$ , and volume 29.79 Å<sup>3</sup> per V<sub>2</sub>H.

I have assigned the hydrogen atoms to certain positions in these crystals with use of general principles determining the structure of metals and intermetallic compounds, and have also found that these principles lead to predicted values of the lattice parameters in good agreement with the observed values.

We may start with the A2 body-centered structure of V, with  $a = 3.027$  Å. There are distorted octahedral interstices in the structure, with one diagonal 3.027 Å long and the other two 4.281 Å long. It is accordingly likely that the hydrogen atoms lie at the centers of these distorted octahedra, form-

ing half-bonds with the two nearer V atoms.

The VHV distance can be predicted. The single-bond radius of V is (3) 1.310 Å and that of H is 0.30 Å. With the half-bond correction (4) 0.18 Å, the expected V-H distance is 1.79 Å and the VHV distance is 3.58 Å, significantly longer than the edge of the unit cube in the element, 3.027 Å. The repeat distance is a sequence VHV VHV VHV. . . is accordingly expected to be 6.61 Å, an increase by 9% caused by the hydrogen atoms.

With tension applied in one direction, it is to be expected that the VHV complexes would be aligned in that direction. One way in which the eight hydrogen atoms might be placed is the diamond arrangement, with each hydrogen atom surrounded tetrahedrally by four hydrogen atoms at the corners of a somewhat elongated tetrahedron. This arrangement, however, leads to a predicted tetragonal unit with  $a = 4.28$  Å and  $c = 6.61$  Å and is ruled out by the observations of Voda *et al.* (1). Another reasonable structure, suggested by Voda *et al.* (1), places four hydrogen atoms at the corners

TABLE I

CRYSTALLOGRAPHIC DATA FOR TETRAGONAL  $\beta_1$ -V<sub>2</sub>H  
(VODA *et al.* (1))

---

Space group No. 141, $D_{4h}^{19} I_4/a_2/m_2/d$
$a = 6.0012(3) \text{ \AA}$ , $c = 6.6188(9) \text{ \AA}$
8H in $(000, \frac{1}{2}\frac{1}{2}\frac{1}{2}) + 000, \frac{1}{2}0\frac{1}{2}, \frac{1}{2}\frac{1}{2}\frac{1}{2}, \frac{1}{2}\frac{1}{2}\frac{1}{2}$
16H in $(000, \frac{1}{2}\frac{1}{2}\frac{1}{2}) + 0xz, \frac{1}{2}\bar{x} + \frac{1}{2}z + \frac{1}{2}, \bar{x}\frac{1}{2}z + \frac{1}{4}, x$ $+ \frac{1}{2}0z + \frac{3}{4}, \frac{1}{2}x\bar{z} + \frac{3}{4}, 0\bar{x} + \frac{1}{2}\bar{z} + \frac{1}{4}, x + \frac{1}{2}\frac{1}{2}\bar{z} + \frac{1}{2},$ $\bar{x}0\bar{z}$
$x = 0.49964(6)$
$z = 0.26712(3)$

---

of a planar rectangle about each hydrogen atom, in the positions given in Table I. With the value of the vanadium parameter given by Voda *et al.* (1), the H–V bond length is 1.768 Å, 0.02 Å less than the predicted value. The H atom also has four other V atoms as neighbors, with H–V = 2.405 Å. Each V atom is surrounded by eight V atoms at the corners of a distorted cube, with four V–V bond lengths 2.558 Å and four 2.691 Å. There are two adjacent vertical edges with lengths 3.083 Å, the other two with 3.536 Å, and two pairs of four lateral edges with 3.001 and 3.009 Å.

The monoclinic form has layers in the *ac* plane that are close to being rhombs, the edges  $a = 4.4566 \text{ \AA}$  and  $c = 4.4760 \text{ \AA}$  being nearly equal (Table II). The long diagonal of the quasi-rhomb, length 6.618 Å, is close to the value expected for all VHV complexes oriented in this direction, 6.61 Å. The short diagonal,  $2 \times 2.9998 \text{ \AA}$ , is slightly contracted from the  $a = 2 \times 3.0006 \text{ \AA}$  of the tetragonal phase, whereas the value of  $b$ , 3.0022 Å, is somewhat larger than the corresponding value  $a = 3.0006 \text{ \AA}$  in the tetragonal phase. With the hydrogen atoms at  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$  and  $00\frac{1}{2}$  (corresponding to centering on *C*, as found by Marsh (2)), and with the values of  $x$  and  $z$  reported by Marsh, the axes of

TABLE II

CRYSTALLOGRAPHIC DATA FOR MONOCLINIC  $\beta_1$ -V<sub>2</sub>H  
(MARSH (2))

---

Space group No. 12, $C_{3h}^3 A112/m$
$a = 4.4566(5) \text{ \AA}$ , $b = 3.0022(2) \text{ \AA}$ , $c = 4.4760(5) \text{ \AA}$ , $\beta = 95.60(5)^\circ$
2H in $2c, 00\frac{1}{2}, \frac{1}{2}\frac{1}{2}\frac{1}{2}$
4V in $4i, x0z, \bar{x}0\bar{z}, x + \frac{1}{2}\frac{1}{2}z, \bar{x} + \frac{1}{2}\frac{1}{2}\bar{z}$
$x = 0.26608(3)$
$z = 0.23373(3)$

---

the VHV complexes lie almost exactly on the long diagonal of the quasi-rhomb in the *ac* plane. The parameter values lead to 1.761 Å for the V–H half-bond length, 0.03 Å less than the predicted value and 0.007 Å less than the value in the tetragonal phase. Each V atom has four V neighbors at 2.690 Å and four at 2.757 Å, in directions nearly the same as in the tetragonal phase.

The foregoing discussion also provides some information about the relative stability of the structures. The hydrogen atom in the VHV linear complex increases the VV distance. The strain that results can be relieved by orienting all the groups in the same direction and changing the lattice constants accordingly, as occurs in both the tetragonal and the monoclinic form. The two forms seem to be nearly equal in stability, with the monoclinic form, with two additional variable lattice constants, the more stable one except when the substance is stretched.

## References

1. Y. VODA, K. MASUMOTO, S. KOIKE, T. SUSUKI, AND S. SATO, *Acta Crystallogr. B* **42**, 529 (1986).
2. R. E. MARSH, *Acta Crystallogr. B* **43**, 415 (1987).
3. L. PAULING AND B. KAMB, *Proc. Natl. Acad. Sci. USA* **83**, 3569 (1986).
4. L. PAULING, *J. Amer. Chem. Soc.* **69**, 542 (1947).