inorganic compounds

A new aquahydroxidocopper(II) oxovanadium(IV) vanadate, Cu(H$_2$O)(OH)VO(VO$_4$)

Jean-Christian Trombe,* Patrick Rozier and Jean Galy

Centre d'Elaboration de Matériaux et d'Etudes Structurales, CNRS, 29 Rue Jeanne Marvig, BP 4347, 31055 Toulouse Cedex 4, France
Correspondence e-mail: trombe@cemes.fr

Single crystals of the title compound have been prepared hydrothermally. Vanadate tetrahedra and distorted oxovanadium octahedra form layers, linked by two independent Cu atoms located on inversion centres. Each Cu atom is surrounded by six O atoms, forming an octahedron distorted by Jahn–Teller elongation. One of the two independent interlayer spaces bridged by the Cu atoms is significantly more compact than the other.

Comment

Many examples are known of anhydrous copper(II) vanadium compounds in which the V atom can be V^V, V^{IV} or of mixed valence (Zavalij & Whittingham, 1999, and references therein). However, hydrated or hydroxido compounds of the same elements are less numerous (Fleury, 1966; Leblanc & Férey, 1990, and references therein). Among these compounds, there exists a natural mineral, Cu$_3$(V$_2$O$_7$)(OH)$_2$·2H$_2$O, called volborthite, whose structure has been determined by X-ray and neutron powder diffraction (Lafontaine *et al.*, 1990). Since this compound has interesting magnetic properties, owing to the peculiar Cu^{II} arrangement characteristic of the Kagomé lattice (Hiroi *et al.*, 2001), we attempted to obtain single crystals by the hydrothermal technique. This experiment failed; however, tiny crystallites were isolated and identified by X-ray powder diffraction as Cu$_4$V$_{2.15}$O$_{9.38}$ (Christian & Muller-Buschbaum, 1975). During attempts to grow single crystals of this latter compound, a new phase was isolated. X-ray single-crystal techniques were used to determine its detailed structure and hence its chemical composition.

In the title compound, the independent non-H atoms are two Cu atoms, located on inversion centres, and two V and seven O atoms, located in general positions. Calculations of the bond-valence sums of atoms Cu1, Cu2, V1 and V2 give values of 2.15, 2.10, 5.01 and 4.19, respectively (Altermatt & Brown, 1985). The excess negative charge is compensated by

the presence of three H atoms, belonging to a water molecule (O7) and a hydroxyl group (O6). The Cu atoms are centred in the (001) and (100) faces of the triclinic cell. A projection view along [100] is given in Fig. 1.

Atom V1 is surrounded by four O atoms that form an almost regular tetrahedron, indicating that the V atom is in the pentavalent state. The V1—O bond distances and the O—V1—O bond angles are in the ranges 1.690 (4)–1.763 (4) Å and 108.3 (2)–110.95 (19)°, respectively (Table 1). Atom V2 exhibits (5+1)-coordination, the O6 atoms of the hydroxido groups completing a distorted octahedron. One of the axial V—O bonds of this octahedron is characteristic of an oxovanadium(IV) or a vanadyl group, VO^{2+} [V2=O5 = 1.617 (4) Å], with V2 displaced by 0.362 (2) Å from the O2^v/O3/O6/O4^{vi} square plane. (Throughout this discussion, superscripts appended to atom names refer to the symmetry operations given in Tables 1 and 2.) The sixth axial distance, V2—O6^{vii}, is correspondingly longer, *i.e.* 2.309 (4) Å. Such distances confirm that atom V2 is in the V^{IV} state, which has a well known tendency to be located in a square pyramid (SP) of O atoms. The V2O$_5$ SP is nearly regular, with V2—O distances in the range 1.959 (4)–2.025 (4) Å in the basal plane and *cis*-O—V2—O angles between these bonds in the range 85.76 (15)–90.38 (15)°.

The V2O$_5$ SPs and V1O$_4$ tetrahedra, which share corners at atoms O2, O3 and O4, form a layer roughly parallel to (001), as shown in Fig. 2. Two such layers, related by the symmetry
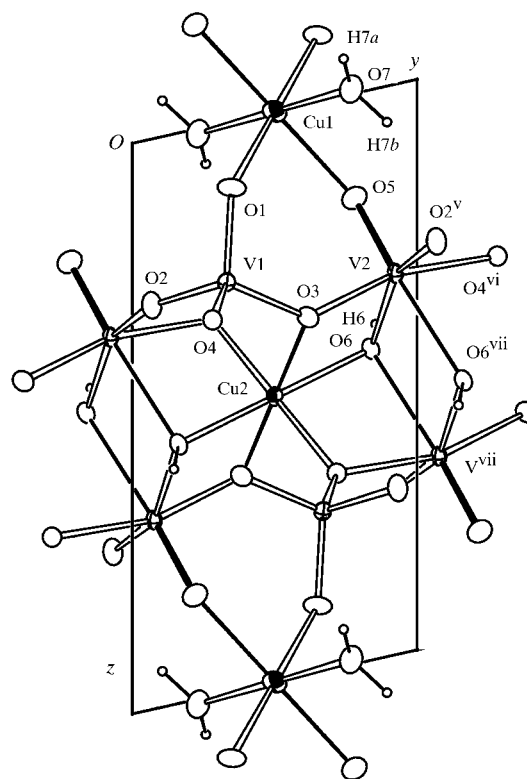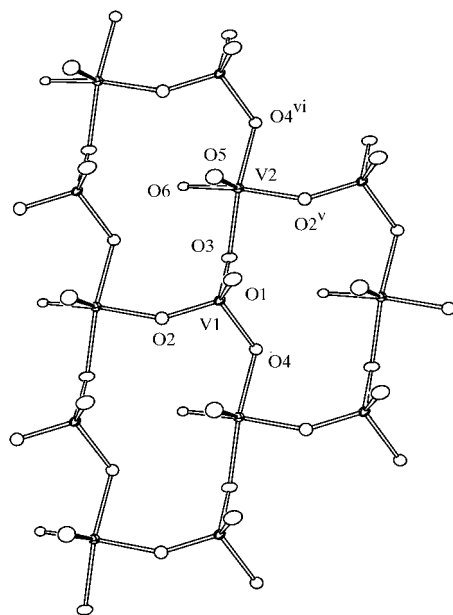

Figure 1
A projection on to (100) of the structure of Cu(H$_2$O)(OH)VO(VO$_4$). Displacement ellipsoids are shown at the 50% probability level. The symmetry codes are as given in Table 1.

centre where atom Cu2 is located, are firmly connected *via* four strong Cu—O bonds (two Cu2—O4 and two Cu2—O6 bonds) and two weaker bonds (two Cu2—O3 bonds), the axial Cu2—O3 bond being rather long [2.534 (4) Å; Table 1]. Cu2 exhibits a sixfold O-atom coordination, thus forming an elongated octahedron with a classic Jahn–Teller distortion. If the longest distance (V2—O6^{vii}) is considered, two V2 atoms, related by a symmetry centre, share the O6–O6^{vii} edge, giving rise to a vanadyl dimer (see Fig. 1), the V2—V2^{vii} distance being 3.492 (2) Å. Note that the vanadyl groups point outward from the thick double layers. Atom O5 of the vanadyl group is linked to atom Cu1, on the symmetry centre $(0,\frac{1}{2},\frac{1}{2})$, at a distance of 2.359 (4) Å. The sixfold coordination around atom Cu1 is completed by atoms O1 and O7. Note again the Jahn–Teller distortion of the Cu1O$_6$ octahedron; the square equatorial plane contains atoms O1 and O7 having short bonds [1.965 (4) and 1.967 (4) Å, respectively], with atom O5 assuming the long axial bond.

The Cu—O distances within the basal planes are similar for the two Cu atoms, but the angles are slightly different. While the O—Cu1—O angles do not depart from 90° by more than 1°, the O—Cu2—O angles range from 84.4 (2) to 95.6 (2)° (Table 1). The opening of the O4^{ii}—Cu2—O6 angle is due mainly to the fact that the two layers of V atoms related by Cu2 are so close [3.049 (1) Å]. The compactness of the space between the two layers can be understood by considering that atoms O3, O4 and O6, located in this space, are μ_3-bridging and concomitantly that the distances between these atoms and the mean plane of the layer are relatively small [0.705 (4), 0.955 (4) and 0.907 (4) Å, respectively]. Atoms O1, O2 and O5, located outside this space, are μ_2-bridging, corresponding to larger distances between atoms O1 and O5 and the mean plane of the layer [1.584 (4) and 1.587 (4) Å respectively]. Consequently, the layers connected by Cu1 atoms are more distant than those related by Cu2 atoms.

Atom H6 of the O6 hydroxido group is approximately in a tetrahedral position with respect to the three metal atoms bound to O6 (Fig. 1); the angles about O6 are in the range 108.6–120.1°. (Note that H6 was refined as a riding atom.) Atom H6 forms a bifurcated hydrogen bond with O2^{vi} and O3^{ii} (Table 2). The water H atoms interact with O1^{viii}, O2^{v} and O1^{v}, with O7···O distances in the range 2.812 (6)–3.138 (6) Å.

Experimental

A few blue–black single crystals were obtained from an aqueous suspension (50 ml) of Cu(SO$_4$)·5H$_2$O, CuO and V$_2$O$_5$ in a 2:2:1 molar ratio. These reactants were sealed in a Teflon-lined steel bomb (autogeneous pressure) and maintained at 473 K for 20 d. After cooling, the precipitate was filtered off, washed with distilled water and dried at room temperature. The X-ray powder pattern of the material shows the presence of a major phase, volborthite, *viz.* Cu$_3$(OH)$_2$(V$_2$O$_7$)·2H$_2$O, and a minor phase, antlerite, *viz.* Cu$_3$(OH)$_4$(SO$_4$).

Crystal data

Cu(H$_2$O)(OH)VO(VO$_4$)	$Z = 2$
$M_r = 280.45$	$D_x = 3.521$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 5.1290$ (7) Å	Cell parameters from 914
$b = 5.3070$ (10) Å	reflections
$c = 10.3590$ (14) Å	$\theta = 6.2$–29.4°
$\alpha = 99.902$ (14)°	$\mu = 7.42$ mm^{-1}
$\beta = 101.139$ (14)°	$T = 293$ (2) K
$\gamma = 101.495$ (13)°	Parallelepiped, blue–black
$V = 264.53$ (8) Å^3	$0.15 \times 0.08 \times 0.05$ mm

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer	914 independent reflections
	819 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.049$
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)	$\theta_{max} = 25.0°$
	$h = -6 \rightarrow 6$
$T_{min} = 0.490$, $T_{max} = 0.690$	$k = -6 \rightarrow 6$
1972 measured reflections	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.032$	$\Delta\rho_{max} = 0.98$ e Å^{-3}
$wR(F^2) = 0.089$	$\Delta\rho_{min} = -0.77$ e Å^{-3}
$S = 1.12$	Extinction correction: *SHELXL*97
914 reflections	Extinction coefficient: 0.012 (3)
95 parameters	
H-atom parameters constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2 + 1.2774P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Figure 2
A view of a layer formed by the vanadate tetrahedra and the oxovanadium square pyramids. The symmetry codes are as given in Table 1.

Direct methods associated with the Patterson function revealed not only the heavy atoms but also, after the first Fourier synthesis, the O-atom sites, leading to a chemical formulation of CuO$_7$V$_2$. Analysis of the Cu and V coordination showed that the charges on the metal atoms were Cu^{2+} and V^{5+}/V^{4+}, implying an electronic imbalance. From difference Fourier syntheses, it was then possible to locate three

inorganic compounds

Table 1
Selected geometric parameters (Å, °).

Cu1—O7	1.965 (4)	V1—O3	1.707 (4)
Cu1—O1^{i}	1.967 (4)	V1—O4	1.763 (4)
Cu1—O5	2.359 (4)	V2—O5	1.617 (4)
Cu2—O4^{ii}	1.953 (3)	V2—O2^{v}	1.959 (4)
Cu2—O6	1.958 (3)	V2—O3	2.008 (4)
Cu2—O3^{iv}	2.534 (4)	V2—O4^{vi}	2.016 (4)
V1—O1	1.690 (4)	V2—O6	2.025 (4)
V1—O2	1.704 (4)	V2—O6^{vii}	2.309 (4)
O7—Cu1—O1^{i}	90.59 (17)	O2^{v}—V2—O3	88.13 (16)
O7—Cu1—O5	91.72 (16)	O5—V2—O4^{vi}	98.45 (18)
O1—Cu1—O5	93.48 (15)	O2^{v}—V2—O4^{vi}	88.55 (16)
O4^{ii}—Cu2—O6	95.63 (15)	O3—V2—O4^{vi}	163.58 (15)
O4^{ii}—Cu2—O3^{iv}	84.89 (14)	O5—V2—O6	102.55 (19)
O6—Cu2—O3^{iv}	105.92 (13)	O2^{v}—V2—O6	154.52 (16)
O1—V1—O2	108.3 (2)	O3—V2—O6	85.76 (15)
O1—V1—O3	109.85 (19)	O4^{vi}—V2—O6	90.38 (15)
O2—V1—O3	110.95 (19)	O5—V2—O6^{vii}	171.22 (17)
O1—V1—O4	109.78 (18)	O2^{v}—V2—O6^{vii}	82.41 (15)
O2—V1—O4	108.75 (18)	O3—V2—O6^{vii}	89.21 (14)
O3—V1—O4	109.19 (18)	O4^{vi}—V2—O6^{vii}	74.42 (13)
O5—V2—O2^{v}	102.8 (2)	O6—V2—O6^{vii}	72.80 (15)
O5—V2—O3	97.96 (18)		

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $1+x, y, z$; (iii) $1-x, 1-y, 1-z$; (iv) $2-x, 1-y, 1-z$; (v) $x, 1+y, z$; (vi) $1+x, 1+y, z$; (vii) $2-x, 2-y, 1-z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O6—H6$\cdots$O2^{vi}	0.99	2.13	2.979 (5)	144
O6—H6$\cdots$O3^{ii}	0.99	2.18	2.967 (5)	136
O7—H7$a\cdots$O1^{viii}	0.89	1.98	2.812 (6)	155
O7—H7$b\cdots$O2^{v}	0.88	2.32	3.114 (6)	151
O7—H7$b\cdots$O1^{v}	0.88	2.43	3.138 (6)	138

Symmetry codes: (ii) $1+x, y, z$; (v) $x, 1+y, z$; (vi) $1+x, 1+y, z$; (viii) $-x, 1-y, -z$.

H atoms, localized on a hydroxido group (O6) and on a water molecule (O7). The H atoms were refined as riding. Refinement of the positional and anisotropic displacement parameters gave a good R factor, the formula $Cu^{2+}V^{5+}V^{4+}O_5(OH)(H_2O)$ being well established, with $Z = 2$ formula units per cell.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

References

Altermatt, D. & Brown, I. D. (1985). *Acta Cryst.* B**41**, 240–244.
Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–37.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Christian, H. P. & Muller-Buschbaum, H. (1975). *Z. Naturforsch. Teil B*, **30**, 175–178.
Fleury, P. (1966). *C. R. Acad. Sci. Ser. C*, **263**, 1375–1377.
Hiroi, Z., Hanawa, M., Kobayashi, N., Nohara, M., Takagi, H., Kato, Y. & Takigawa, M. (2001). *J. Phys. Soc. Jpn*, **70**, 3377–3384.
Lafontaine, M. A., Le Bail, A. & Férey, G. (1990). *J. Solid State Chem.* **85**, 220–227.
Leblanc, M. & Férey, G. (1990). *Acta Cryst.* C**46**, 15–18.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Zavalij, P. Y. & Whittingham, M. S. (1999). *Acta Cryst.* B**55**, 627–663.