L'uranium est entouré d'un octaèdre aplati composé de quatre oxygènes dans le plan des feuillets et une liaison uranyle O(3)—U—O(3) pratiquement perpendiculaire de 1,79 Å. Le magnésium est également au centre d'un octaèdre et dans le plan des feuillets, les polyèdres MgO_6 et UO_6 sont liés entre eux par une arête et un sommet. Les atomes de bore sont au centre de triangles plans reliés par paires par l'atome O(5). Ils sont joints par les sommets aux octaèdres entourant le magnésium et par l'arête O(1)—O(4) aux polyèdres entourant l'uranium. Les atomes O(1), O(2), O(4) et O(6) sont donc communs à trois cations. Dans la direction perpendiculaire, la cohésion de la structure est assurée par les atomes O(3) qui relient dans la direction *z* les octaèdres UO_6 et MgO_6, formant des chaînes Mg—O—U. Cette disposition en feuillets explique bien la forme des cristaux aplatis selon [00*z*] et toutes les distances sont conformes aux normes habituelles.

Enfin, le point commun entre ce diborouranate et $CaB_2U_2O_{10}$ (Gasperin, 1987) est qu'ils contiennent tous deux des entités $(B_2O_5)^{4-}$ rencontrées pour la première fois dans $TlNbB_2O_6$ (Gasperin, 1974).

Références

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1963). *ORFLS*. Rapport ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, Etats-Unis.

GASPERIN, M. (1974). *Acta Cryst.* **B30**, 1180–1183.

GASPERIN, M. (1987). *Acta Cryst.* **C43**, 1247–1250.

HOEKSTRA, H. R. (1967). *Lanthanides/Actinides Chemistry, Advances in Chemistry Series* No. 71, edité par R. F. GOULD, pp. 320–330. Washington, DC: American Chemical Society.

International Tables for X-ray Crystallography (1974). Tome IV. Birmingham: Kynoch Press. (Distributeur actuel D. Reidel, Dordrecht.)

MEULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014–1018.

Acta Cryst. (1987). C**43**, 2266–2268

Structure of Barium Metavanadate Monohydrate

BY Ľ. ULICKÁ

Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University,
842 15 *Bratislava, Czechoslovakia*

F. PAVELČÍK

Department of Analytical Chemistry, Faculty of Pharmacy, Comenius University,
832 32 *Bratislava, Czechoslovakia*

AND K. HUML

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 *Prague* 6, *Czechoslovakia*

(*Received* 21 *April* 1987; *accepted* 27 *July* 1987)

Abstract. $Ba(VO_3)_2.H_2O$, $M_r = 353{\cdot}22$, orthorhombic, $P2_12_12_1$, $a = 8{\cdot}997\,(2)$, $b = 9{\cdot}728\,(2)$, $c = 7{\cdot}409\,(1)$ Å, $V = 648{\cdot}5\,(2)$ Å^3, $Z = 4$, $D_m = 3{\cdot}604$, $D_x = 3{\cdot}617$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 91{\cdot}375$ cm^{-1}, $F(000) = 640$, room temperature, $R = 0{\cdot}039$ for 1310 independent reflections. Each V atom is coordinated by four O atoms forming a tetrahedron which is connected with others to form a twisted spiral parallel to **c**. The Ba atom is coordinated by nine O atoms and one water molecule.

Introduction. The common structural feature of the hydrated metavanadates determined so far is the presence of chains formed by connection of VO_5 polyhedra. Fivefold V coordination was found by Christ, Clark & Evans (1954) in $KVO_3.H_2O$, by Kelsey & Barnes (1962) in $Ca(VO_3)_2.2H_2O$, by Ahmed & Barnes (1963) in $Ca(VO_3)_2.4H_2O$, by Sedlacek & Dornberger-Schiff (1965) in $Sr(VO_3)_2.4H_2O$, by Safjanov, Bočkova, Kuzmin & Belov (1976) in $Co(VO_3)_2.4H_2O$ and by Ulická (1987) in $Cd(VO_3)_2.4H_2O$. This uniformity of the VO_5 polyhedra is particularly surprising in the case of $KVO_3.H_2O$ since, according to Petrášová, Maďar & Hanic (1958), anhydrous KVO_3 consists of chains of VO_4 tetrahedra. Fourfold O-atom coordination of V atoms is also typical for the other anhydrous metavanadates of composition $M^{\rm I}VO_3$. It is therefore desirable to examine the factors which influence the coordination number of vanadium in the metavanadates, since the small number of available structure determinations does not provide conclusive information. The crystal structure of

0108-2701/87/122266-03$01.50

Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses for* $Ba(VO_3)_2.H_2O$

$$B_{eq} = \tfrac{4}{3} \sum_{i=1}^{3} B_{ii} a_i^2.$$

	x	y	z	B_{eq}
Ba	999 (1)	5206 (1)	7447 (1)	1·19
V(1)	−47 (1)	−46 (1)	2705 (1)	1·05
V(2)	2666 (1)	1769 (1)	4654 (1)	1·08
O(1)	−1227 (6)	−1043 (5)	3821 (8)	1·22
O(2)	−1043 (7)	920 (6)	1350 (8)	1·48
O(3)	907 (6)	914 (6)	4449 (7)	1·38
O(4)	1261 (7)	−1035 (6)	1430 (9)	1·84
O(5)	2375 (6)	3407 (6)	5095 (7)	1·47
O(6)	3640 (6)	1723 (6)	2800 (8)	1·69
O(7)	1387 (8)	1801 (8)	−1213 (10)	2·60

$Ba(VO_3)_2.H_2O$ presented here provides further relevant structural data.

Experimental. Single crystal obtained according to Žurková, Čorba & Suchá (1968), $0{\cdot}10 \times 0{\cdot}18 \times 0{\cdot}21$ mm; D_m by flotation in Clerici solution; systematic absences and space group from Weissenberg photographs; Syntex $P2_1$ diffractometer; unit-cell parameters by least-squares fit of positional angles of 25 reflections with $21 < 2\theta < 38°$. Graphite monochromator, Mo $K\alpha$ radiation; ω–2θ scan mode, variable scan rate 1·5 to 29·3° $2\theta\,\mathrm{min}^{-1}$; three standard reflections monitored every 47 reflections, no significant systematic fluctuation; background at each end of the scan for one half of the scan time; 1615 measured reflections with $3{\cdot}5 \le 2\theta \le 67°$ ($h = 0$–14, $k = 0$–15, $l = 0$–11). Intensities corrected for empirical absorption based on 13 reflections and their symmetry equivalents; 1019 ψ measurements (Flack, 1977) (max., min. transmission 1·17, 0·80). Mean R_{int} for ψ intensities dropped from 11·8 to 5·7%. 1483 unique, 1310 observed [$|F_o| > 3\sigma(F)$] reflections. Structure solved by Patterson and Fourier methods with *XFPS*86 (Pavelčík, 1986). Refinement on $|F_o|$ by full-matrix least squares with anisotropic thermal parameters; $R = 0{\cdot}0394$, $wR = 0{\cdot}0495$ for observed data, $R = 0{\cdot}0437$ for all reflections; $(\Delta/\sigma)_{max} = 0{\cdot}07$; weighting scheme $w^{-1} = \sigma^2(F) + (0{\cdot}04\,|F_o|)^2$; scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1969); anomalous dispersion for Ba and V atoms; $S = 0{\cdot}62$; $(\Delta\rho)_{max} = 1{\cdot}29$, $(\Delta\rho)_{min} = -0{\cdot}97$ e Å^{-3}. H atoms were not located. Final atomic coordinates and equivalent isotropic temperature factors are given in Table 1.*

Discussion. The crystal structure of $Ba(VO_3)_2.H_2O$ projected onto the (001) plane is shown in Fig. 1. The metavanadate anion is formed by VO_4 tetrahedra which are connected by means of common O(3) and O(4) atoms into infinite twisted spiral chains along **c**, as depicted in Fig. 2. The bond lengths between V and the O atoms shared by two neighbouring VO_4 tetrahedra are much longer than those between V and unshared O atoms (see Table 2). This phenomenon is obviously caused by repulsive forces between V(1) and V(2).

The interatomic V—O distances and O—V—O bond angles listed in Table 2 indicate two types of differently distorted VO_4 tetrahedra. The O—V—O angles show that the distortion of the tetrahedron centred on V(1) is somewhat greater than that centred on V(2). This might

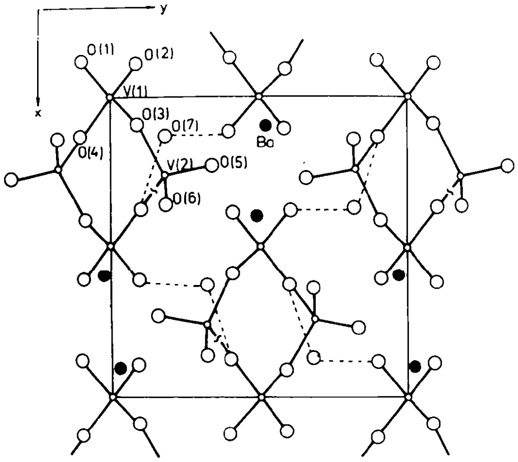

Fig. 1. Projection of $Ba(VO_3)_2.H_2O$ crystal structure onto the (001) plane.

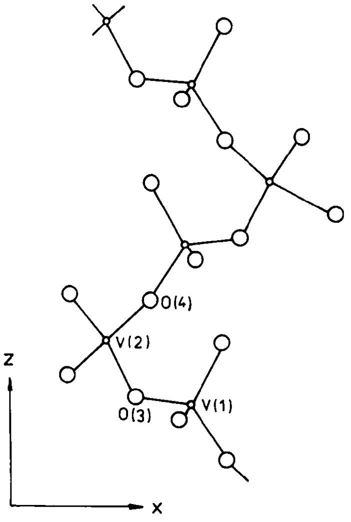

Fig. 2. Spiral chain in $Ba(VO_3)_2.H_2O$.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44279 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses for* $Ba(VO_3)_2.H_2O$

Ba–O(1^{i})	2·789 (5)	V(1)–O(1)	1·658 (5)
Ba–O(1^{v})	3·027 (6)	V(1)–O(2)	1·643 (6)
Ba–O(2^{ii})	2·899 (6)	V(1)–O(3)	1·812 (5)
Ba–O(2^{i})	3·012 (6)	V(1)–O(4)	1·789 (6)
Ba–O(3^{v})	2·949 (5)	V(2)–O(3)	1·795 (6)
Ba–O(5^{iii})	2·794 (5)	V(2)–O(4^{iii})	1·781 (6)
Ba–O(5)	2·763 (6)	V(2)–O(5)	1·647 (6)
Ba–O(6^{iii})	3·016 (6)	V(2)–O(6)	1·630 (6)
Ba–O(6^{iv})	2·840 (6)		
Ba–O(7^{ii})	2·802 (7)		
O(1)–V(1)–O(2)	106·8 (2)	O(5)–V(2)–O(6)	106·2 (2)
O(1)–V(1)–O(3)	104·4 (2)	O(5)–V(2)–O(4^{iii})	109·1 (2)
O(1)–V(1)–O(4)	111·7 (2)	O(5)–V(2)–O(3)	108·9 (2)
O(2)–V(1)–O(3)	113·5 (2)	O(6)–V(2)–O(3)	112·9 (2)
O(2)–V(1)–O(4)	110·1 (3)	O(6)–V(2)–O(4^{iii})	108·7 (2)
O(3)–V(1)–O(4)	110·0 (2)	O(3)–V(2)–O(4^{iii})	110·7 (2)
V(1)–O(3)–V(2)	135·8 (3)	V(1)–O(4)–V(2^{vi})	164·0 (4)

Symmetry code: (i) $0·5+x, 0·5-y, -z$; (ii) $-x, 0·5+y, 0·5-z$; (iii) $0·5-x, -y, 0·5+z$; (iv) $x-0·5, 0·5-y, -z$; (v) $-x, 0·5+y, 1·5-z$; (vi) $0·5-x, -y, z-0·5$.

be explained by the formation of an H bond between the H_2O molecule, O(7), and the terminal O atom of the V(1) polyhedron. The second H bond formed between O(7) and the bridging O atom does not greatly affect the symmetry of the V(2) tetrahedron. The H bonds are postulated from the interatomic distances O(1^{ii})···O(7) and O(4^{iii})···O(7) which are 2·749 (9) and 2·842 (10) Å, respectively; the angle O(1^{ii})···O(7)···O(4^{iii}) is 129·4 (3)°.

Interatomic distances and bond angles in the VO_4 tetrahedra are in good agreement with those found by Petrášová, Maďar & Hanic (1958), Syneček & Hanic (1954), Shannon & Calvo (1973), Marumo, Isobe & Iwai (1974) and Ganne, Piffard & Tournoux (1974) in the structures of KVO_3, NH_4VO_3, $LiVO_3$, $NaVO_3$ and $TlVO_3$, respectively.

The Ba atom in the structure of $Ba(VO_3)_2.H_2O$ is surrounded by nine O atoms of the neighbouring VO_4 polyhedra and by one water molecule, forming an irregular polyhedron. Only Ba—O distances less than 3·10 Å are taken into account; the next smallest Ba···O distance is 3·475 (8) Å.

The crystal structure of $Ba(VO_3)_2.H_2O$ has no analogue amongst hydrated metavanadates; the fourfold vanadium coordination observed here represents an exception from the above-mentioned uniformity of vanadium–oxygen chains. Its unique feature is the spiral twisted anion chain which has not been found so far in any other metavanadate structure.

References

Ahmed, F. R. & Barnes, W. H. (1963). *Can. Mineral.* **7**, 713–726.

Christ, C. L., Clark, J. R. & Evans, H. T. Jr (1954). *Acta Cryst.* **7**, 801–807.

Flack, H. D. (1977). *Acta Cryst.* A**33**, 890–898.

Ganne, M., Piffard, Y. & Tournoux, M. (1974). *Can. J. Chem.* **52**, 3539–3543.

International Tables for X-ray Crystallography (1969). Vol. III. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Kelsey, C. H. & Barnes, W. H. (1962). *Can. Mineral.* **6**, 448–466.

Marumo, F., Isobe, M. & Iwai, S. (1974). *Acta Cryst.* B**30**, 1628–1630.

Pavelčík, F. (1986). *J. Appl. Cryst.* **19**, 488–491.

Petrášová, M., Maďar, J. & Hanic, F. (1958). *Chem. Zvesti*, **12**, 410–418.

Safjanov, J. N., Bočkova, P. I., Kuzmin, E. A. & Belov, N. V. (1976). *Dokl. Akad. Nauk SSSR*, **226**, 574–576.

Sedlacek, P. & Dornberger-Schiff, K. (1965). *Acta Cryst.* **18**, 407–410.

Shannon, R. D. & Calvo, C. (1973). *Can. J. Chem.* **51**, 265–273.

Syneček, V. & Hanic, F. (1954). *Czech. J. Phys.* **4**, 120–130.

Ulická, Ľ. (1987). *Chem. Zvesti.* In the press.

Žurková, Ľ., Čorba, J. & Suchá, V. (1968). *Chem. Zvesti*, **22**, 73–76.

Acta Cryst. (1987). C**43**, 2268–2270

Structure de l'Octatellurure de Diarsenic et de Pentagermanium

Par S. Jaulmes, Han Wan Shu et A. Mazurier

Laboratoire de Chimie Minérale Structurale associé au CNRS UA 200 (*Laboratoire de Physique*), *Faculté des Sciences Pharmaceutiques et Biologiques, Paris-Luxembourg,* 4, *Avenue de l'Observatoire,*
75270 *Paris CEDEX* 06, *France*

(*Reçu le* 13 *mars* 1987; *accepté le* 6 *août* 1987)

Abstract. $As_2Ge_5Te_8$, $M_r = 1533·6$, trigonal, $P\bar{3}m1$, $a = 4·114$ (1), $c = 27·56$ (1) Å, $V = 403·9$ (4) Å^3, $Z = 1$, $D_x = 6·30$, $D_m = 6·2$ (2) Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 28·74$ mm^{-1}, $F(000) = 642$, $T = 293$ K, $R = 0·0508$ for 395 independent reflections. The structure consists of one sheet of As_2Te_3 and five sheets of composition GeTe in which all the atoms have octahedral coordination.

0108-2701/87/122268-03$01.50