Symmetry codes: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $-x, -y, -z$; (v) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (vi) $1 + x, y, z$; (vii) $1 - x, -y, 1 - z$; (viii) $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$; (ix) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

Table 3. *Refined displacement parameters* (Å^2)

The form of the anisotropic displacement parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	0.0013 (1)	0.0017 (1)	0.0021 (1)	0.0004 (2)	0.0004 (2)	−0.0001 (3)
Mo(2)	0.0016 (1)	0.0016 (1)	0.0022 (1)	0.0003 (2)	0.0006 (2)	0.0004 (3)
P(1)	0.0019 (4)	0.0022 (4)	0.0027 (4)	−0.0001 (6)	0.0023 (7)	−0.0002 (7)
P(2)	0.0026 (3)	0.0012 (3)	0.0017 (4)	−0.0006 (6)	0.0016 (6)	0.0001 (7)
Tl(1)	0.00373 (8)	0.00425 (9)	0.00384 (9)	−0.0010 (2)	−0.0009 (2)	−0.0016 (2)
Tl(2)	0.00808 (9)	0.00564 (8)	0.0144 (2)	−0.0024 (2)	0.0038 (2)	−0.0025 (2)
Tl(3)	0.0153 (3)	0.0162 (3)	0.0050 (2)	0.0206 (4)	0.0078 (4)	0.0067 (5)

Calculations were performed using a MicroVAX II computer with the *SDP* system (Frenz, 1982). Drawings were prepared using *STRUPLO*84 (Fisher, 1985).

Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71289 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1040]

References

Fisher, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.
B. A. Frenz & Associates, Inc. (1982). *SDP Structure Determination Package*. College Station Texas, USA.
Gueho, C., Borel, M. M., Grandin, A., Leclaire, A. & Raveau, B. (1993). *J. Solid State Chem.* **104**, 202–208.

Acta Cryst. (1993). C49, 1879–1881

Structure of $Sr_3V_{10}O_{28}.22H_2O$

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(*Received* 14 *October* 1992; *accepted* 2 *April* 1993)

Abstract

The crystal structure of hydrated strontium decavanadate, $Sr_3V_{10}O_{28}.22H_2O$, has been determined. It contains two types of strontium ions: the first is coordinated to seven water molecules which define a pentagonal bipyramid; the second bonds to five molecules of water and three O atoms of different decavanadate ions, thereby bridging between decavanadate ions to produce layers of formula $[Sr_2V_{10}O_{38}H_{20}]_n$ on the crystallographic plane (100). The heptacoordinated Sr and the five molecules of water associated with it are located between the different layers.

Comment

The complicated chemistry which arises from the condensation reactions of aqueous vanadate ions and other transition-metal oxo anions depends on the pH of the solution in which the reactions occur. The more acidic the solution the greater is the molecular weight of the isopolynuclear complex anions formed. The following vanadates may be obtained: orthovanadates (pH > 12.6), pyrovanadates (pH 12.6–9.6), metavanadates (pH 9.6–6.5), polyvanadates (pH 6.5–2) and pervanadyl (pH < 0.8). Among the polyvanadates, the decavanadates (salts of the $V_{10}O_{28}^{6-}$ ion) have particular mining and chemical interest as they are found in uranium ores.

Norblad (1875) described $Ba_3V_{10}O_{28}.19H_2O$ among other polyvanadates. The crystal structures of synthetic and natural forms of pascoite $Ca_3V_{10}O_{28}.17H_2O$ have been determined (Marvin & Magin, 1959; Swallow, Ahmed & Barnes, 1966), as have those of double salts like $K_2Mg_2V_{10}O_{28}.16H_2O$, $Cs_2Mg_2V_{10}O_{28}.16H_2O$ and $K_2Zn_2V_{10}O_{28}.16H_2O$ (Weeks, Cisney & Sherwood, 1951; Evans, 1966) and that of the protonated species $[(C_6H_5)_4P]_3H_3V_{10}O_{28}.4CH_3CN$ (Day, Klemperer & Maltbie, 1987).

The title compound was prepared by the addition of excess vanadium pentoxide to a suspension of strontium hydroxide in boiling water, adjusting the pH to about 5 with acetic acid, until the solution became ochre in colour, followed by immediate filtration and crystallization of the filtrate. Crystals were obtained from solutions in distilled water and dried in air at room temperature. Vanadium content was determined spectrophotometrically by the peroxide method (Sandell, 1950) and the strontium content was determined by microgravimetry, giving a chemical analysis and atomic ratio V:Sr = 9.9:3.0. The empirical formula is also consistent with elemental analyses for O and H.

The Sr(1) atom has a B_{eq} value double that of Sr(2). Refinement of its occupancy factor led to a value of 1; slight disorder of this atom around the twofold axis may explain its relatively large B_{eq} value. As only five H atoms were observed in difference syntheses, it was difficult to distinguish between oxide and water O atoms. The presence of

OH groups is considered unlikely since the compound was obtained from an acidic solution. Water O atoms have been assumed to be associated with Sr atoms, which have greater basic character than V ions. This assumption agrees with the observed positions of H atoms and with O—metal and H bond lengths.

The anion straddles a crystallographic diad axis. At its centre there is a condensed system of two distorted octahedra which have coplanar equatorial planes and a shared edge, V(1)—V(1′). Each V atom is coordinated to six O atoms to make up the decavanadate group which consists of ten VO_6 octahedra sharing edges. V—O bond lengths and angles are similar to those obtained for the decavanadate ion in the previous crystal-structure determination. The two independent Sr ions show different types of coordination: Sr(1) is coordinated to seven water molecules which define a pentagonal bipyramid, whereas Sr(2) is bonded to three O atoms from different decavanadate ions and to five water molecules, displaying square antiprismatic coordination. This behaviour is different to that observed in the double salts, where the Zn or Mg ion is coordinated to six water molecules, and in the Ca complex where Ca(2) is linked to seven water molecules and Ca(1) to five water molecules and two decavanadate O atoms. Thus, we conclude that the charge-to-radius ratio of the counter cation determines the number of hydrate water molecules of the complex.

Kempf, Rohmer, Poblet, Bo & Benard (1992) have reported a theoretical analysis of the relative basicities of the O-atom sites in the decavanadate ion, and they conclude that site *B* [according to the nomenclature of Day, Klemperer & Maltbie (1987) for the O atoms of the decavanadate ion] is the most attractive site for protons or small cationic groups. However, the intermolecular distances observed in decavanadate structures show that the volume and the acidity of the counter cation are more important in defining the packing of the crystal than the basicity of the O-atom sites of the decavanadate ion.

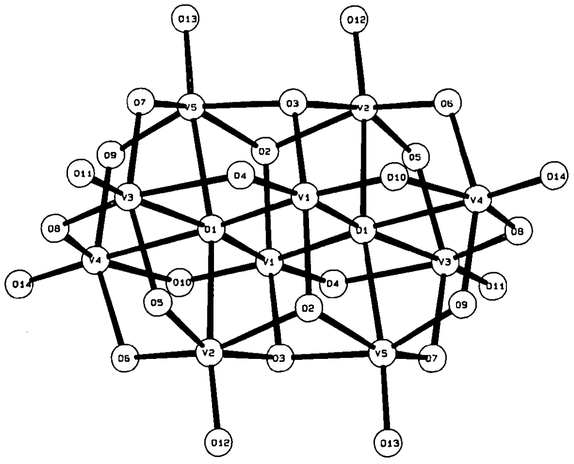

Fig. 1. View of the decavanadate ion showing the atom numbering.

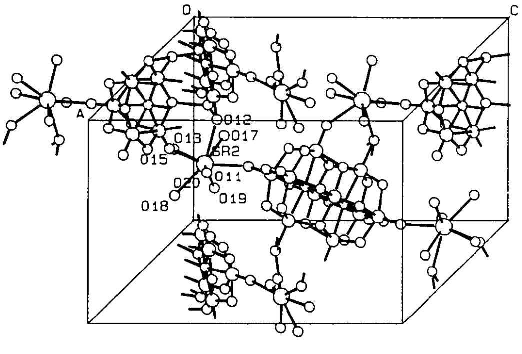

Fig. 2. View of the bridging of decavanadate ions by the pentaaquo strontium cation with the unit-cell boundaries indicated.

Experimental

Crystal data

$Sr_3V_{10}O_{28}.22H_2O$
$M_r = 1616.60$
Monoclinic
$C2/c$
$a = 18.839\ (2)$ Å
$b = 12.719\ (1)$ Å
$c = 18.743\ (2)$ Å
$\beta = 109.55\ (2)°$
$V = 4232\ (1)$ Å^3
$Z = 4$

$D_x = 2.536$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 8$-$14°$
$\mu = 6.383$ mm^{-1}
$T = 298$ K
Prism
$0.2 \times 0.1 \times 0.1$ mm
Ochre

Data collection

Philips PW1100 diffractometer
ω scans
Absorption correction: *DIFABS* (Walker & Stuart, 1983)
$T_{\min} = 0.37$, $T_{\max} = 0.40$
4300 measured reflections
3462 observed reflections $[I > 2.5\sigma(I)]$

$R_{\rm int} = 0.021$
$\theta_{\max} = 30°$
$h = -24 \rightarrow 24$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 26$
3 standard reflections
frequency: 120 min
intensity variation: not significant

Refinement

Refinement on F
Final $R = 0.031$
$wR = 0.033$
3462 reflections
302 parameters
$w = (\sigma^2 F_o + 0.0016 F_o^2)^{-1}$
$(\Delta/\sigma)_{\max} = 0.1$

$\Delta\rho_{\max} = 0.6$ e Å^{-3}
$\Delta\rho_{\min} = -0.4$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Sr(1)	0.0	0.04562 (4)	0.25000	3.41 (3)
Sr(2)	0.13040 (2)	0.65750 (2)	0.07854 (2)	1.59 (2)
V(1)	0.16755 (3)	0.78506 (4)	0.44031 (3)	1.15 (2)
V(2)	0.31573 (3)	0.84172 (4)	0.40721 (3)	1.23 (2)
V(3)	0.20664 (3)	0.66805 (4)	0.31428 (3)	1.54 (2)
V(4)	0.36075 (3)	0.60532 (4)	0.42538 (3)	1.53 (2)
V(5)	0.21578 (3)	0.54841 (4)	0.46104 (3)	1.27 (2)
O(1)	0.2641 (1)	0.7015 (2)	0.4427 (1)	1.05 (8)
O(2)	0.2298 (1)	0.8995 (2)	0.4335 (1)	1.32 (8)
O(3)	0.1455 (1)	0.6540 (2)	0.4781 (1)	1.38 (8)
O(4)	0.1307 (1)	0.7577 (2)	0.3478 (1)	1.61 (9)
O(5)	0.2515 (1)	0.8015 (2)	0.3153 (1)	1.54 (8)
O(6)	0.3880 (1)	0.7436 (2)	0.4104 (1)	1.70 (9)
O(7)	0.1702 (1)	0.5600 (2)	0.3583 (1)	1.60 (9)
O(8)	0.2945 (1)	0.5998 (2)	0.3271 (1)	1.71 (9)
O(9)	0.3051 (1)	0.5026 (2)	0.4547 (1)	1.44 (8)
O(10)	0.1028 (1)	0.8561 (2)	0.4642 (1)	1.68 (8)
O(11)	0.1589 (2)	0.6541 (2)	0.2265 (1)	2.32 (11)
O(12)	0.3524 (2)	0.9496 (2)	0.3909 (2)	2.14 (10)
O(13)	0.1788 (1)	0.4421 (2)	0.4812 (1)	1.64 (9)
O(14)	0.4318 (2)	0.5393 (2)	0.4202 (2)	2.69 (12)
O(15)	0.0241 (2)	0.6384 (2)	−0.0567 (2)	2.95 (12)
O(16)	0.2242 (3)	0.8355 (4)	0.1623 (3)	6.81 (28)
O(17)	−0.0053 (2)	0.4179 (2)	−0.0974 (2)	2.78 (12)
O(18)	0.3247 (2)	0.7092 (2)	0.0024 (2)	3.58 (15)
O(19)	0.0535 (2)	0.8156 (3)	0.0834 (4)	7.29 (25)
O(20)	0.2736 (2)	0.6283 (4)	0.1331 (2)	5.75 (21)
O(21)	−0.0686 (2)	1.0645 (4)	0.1116 (2)	5.34 (20)
O(22)	0.0788 (3)	1.2013 (3)	0.2321 (3)	4.92 (21)
O(23)	0.1314 (2)	0.9767 (3)	0.2564 (3)	5.72 (23)
O(24)	0.0	0.8457 (6)	0.2500	10.65 (50)
O(25)	0.0737 (3)	0.3791 (3)	0.3128 (3)	5.33 (21)
O(26)	0.0	0.5866 (7)	0.2500	7.17 (41)

Table 2. *Geometric parameters* (Å, °)

O(21)—Sr(1)	2.493 (4)	O(6)—V(2)	1.833 (2)
O(22)—Sr(1)	2.562 (4)	O(12)—V(2)	1.611 (2)
O(23)—Sr(1)	2.591 (4)	O(3^{v})—V(2)	2.026 (2)
O(24)—Sr(1)	2.543 (7)	O(1)—V(3)	2.324 (2)
O(11)—Sr(2)	2.643 (3)	O(4)—V(3)	2.084 (2)
O(15)—Sr(2)	2.664 (3)	O(5)—V(3)	1.893 (2)
O(19)—Sr(2)	2.498 (3)	O(7)—V(3)	1.850 (2)
O(20)—Sr(2)	2.571 (3)	O(8)—V(3)	1.812 (3)
O(17^{i})—Sr(2)	2.675 (3)	O(11)—V(3)	1.599 (3)
O(13^{ii})—Sr(2)	2.623 (3)	O(1)—V(4)	2.305 (2)
O(18^{iii})—Sr(2)	2.597 (3)	O(6)—V(4)	1.880 (2)
O(12^{iv})—Sr(2)	2.702 (3)	O(8)—V(4)	1.848 (2)
O(1)—V(1)	2.094 (2)	O(9)—V(4)	1.869 (2)
O(2)—V(1)	1.901 (2)	O(14)—V(4)	1.610 (3)
O(3)—V(1)	1.911 (2)	O(10^{v})—V(4)	2.011 (3)
O(4)—V(1)	1.675 (2)	O(1)—V(5)	2.224 (2)
O(10)—V(1)	1.694 (2)	O(3)—V(5)	1.985 (2)
O(1^{v})—V(1)	2.146 (2)	O(7)—V(5)	1.833 (2)
O(1)—V(2)	2.237 (2)	O(9)—V(5)	1.822 (2)
O(2)—V(2)	1.984 (2)	O(13)—V(5)	1.623 (2)
O(5)—V(2)	1.816 (2)	O(2^{v})—V(5)	2.010 (2)
O(21^{vi})—Sr(1)—O(21)	168.9 (2)	O(22)—Sr(1)—O(21)	84.9 (2)
O(21^{vi})—Sr(1)—O(22)	86.6 (2)	O(22^{vi})—Sr(1)—O(22)	78.8 (2)
O(23)—Sr(1)—O(21)	103.6 (1)	O(21^{vi})—Sr(1)—O(23)	80.2 (2)
O(23)—Sr(1)—O(22)	71.4 (1)	O(22^{vi})—Sr(1)—O(23)	147.3 (1)
O(23^{vi})—Sr(1)—O(23)	140.5 (1)	O(24)—Sr(1)—O(21)	95.5 (1)
O(24)—Sr(1)—O(22)	140.6 (1)	O(24)—Sr(1)—O(23)	70.2 (1)
O(12^{iv})—Sr(2)—O(11)	78.1 (2)	O(13^{ii})—Sr(2)—O(11)	136.6 (2)
O(13^{ii})—Sr(2)—O(12^{iv})	68.3 (2)	O(15)—Sr(2)—O(11)	145.2 (1)
O(15)—Sr(2)—O(12^{iv})	96.4 (2)	O(15)—Sr(2)—O(13^{ii})	67.6 (1)
O(17^{i})—Sr(2)—O(11)	74.6 (2)	O(17^{i})—Sr(2)—O(12^{iv})	70.7 (1)
O(17^{i})—Sr(2)—O(13^{ii})	116.4 (1)	O(17^{i})—Sr(2)—O(15)	71.2 (1)
O(18^{iii})—Sr(2)—O(11)	129.2 (1)	O(18^{iii})—Sr(2)—O(12^{iv})	136.3 (1)
O(18^{iii})—Sr(2)—O(13^{ii})	69.6 (1)	O(18^{iii})—Sr(2)—O(15)	78.0 (1)
O(18^{iii})—Sr(2)—O(17^{i})	141.6 (2)	O(19)—Sr(2)—O(11)	83.8 (1)
O(19)—Sr(2)—O(12^{iv})	144.1 (1)	O(19)—Sr(2)—O(13^{ii})	139.0 (1)
O(19)—Sr(2)—O(15)	81.2 (1)	O(19)—Sr(2)—O(17^{i})	74.7 (1)
O(19)—Sr(2)—O(18^{iii})	78.6 (1)	O(20)—Sr(2)—O(11)	76.3 (1)
O(20)—Sr(2)—O(12^{iv})	74.9 (2)	O(20)—Sr(2)—O(13^{ii})	69.2 (1)
O(20)—Sr(2)—O(15)	136.0 (1)	O(20)—Sr(2)—O(17^{i})	138.5 (1)
O(20)—Sr(2)—O(18^{iii})	79.8 (1)	O(20)—Sr(2)—O(19)	130.2 (1)

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $x, 1-y, z-\frac{1}{2}$; (iii) $\frac{1}{2}-x, \frac{3}{2}-y, -z$; (iv) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (v) $\frac{1}{2}-x, \frac{3}{2}-y, 1-z$; (vi) $-x, y, \frac{1}{2}-z$.

CFEO (Solans, 1978) was used for data reduction. The structure was solved by Patterson synthesis using *SHELXS*86 (Sheldrick, 1990) and refined by full-matrix least squares using *SHELX*76 (Sheldrick, 1976). Molecular views were obtained using versions of *PLUTO* (Motherwell & Clegg, 1978) and *ORTEP* (Johnson, 1976) adapted for a PC (Brueggemann & Schmid, 1990).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71232 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1037]

References

Brueggemann, R. & Schmid, G. (1990). PC version of *ORTEP*3.2 and *PLUTO*4.1. Univ. of Ulm, Germany.

Day, V. W., Klemperer, W. G. & Maltbie, D. J. (1987). *J. Am. Chem. Soc.* **109**, 2991–3002.

Evans, H. T. Jr (1966). *Inorg. Chem.* **5**, 967–977.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kempf, J. Y., Rohmer, M. M., Poblet, J. M., Bo, C. & Bènard, M. (1992). *J. Am. Chem. Soc.* **114**, 1136–1145.

Marvin, R. & Magin, G. B. Jr (1959). *US Geol. Survey Prof. Paper*, **320**, 107–110.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures.* Univ. of Cambridge, England.

Norblad, J. A. (1875). *Bull. Soc. Chim. Fr.* **24**(2), 64–71.

Sandell, E. B. (1950). *Colorimetric Determination of Trace Metals*, Vol. III. pp 609–611. New York: Interscience.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Solans, X. (1978). *CFEO.* Univ. of Barcelona, Spain.

Swallow, A. G., Ahmed, F. R. & Barnes, W. H. (1966). *Acta Cryst.* **21**, 397–405.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Weeks, A. D., Cisney, E. A. & Sherwood, A. M. (1951). *Am. Mineral.* **36**, 326–343.