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References

ANDERSSON, Y. (1977). *Acta Chem. Scand. Ser. A*, **31**, 354–358.

ANDERSSON, Y., KAEWCHANSILP, V., DEL ROSARIO CASTELEIRO SOTO, M. & RUNDQVIST, S. (1974). *Acta Chem. Scand. Ser. A*, **28**, 797–802.

ANDERSSON, Y., RUNDQVIST, S., TELLGREN, R., THOMAS, J. O. & FLANAGAN, T. B. (1980). *J. Solid State Chem.* **32**, 321–327.

ARONSSON, B., BÄCKMAN, M. & RUNDQVIST, S. (1960). *Acta Chem. Scand.* **14**, 1001–1005.

BOLLER, H. & NOWOTNY, H. (1967). *Monatsh. Chem.* **98**, 2127–2132.

CARLSSON, B., GÖLIN, M. & RUNDQVIST, S. (1973). *J. Solid State Chem.* **8**, 57–67.

DESLATTES, R. D. & HENINS, A. (1973). *Phys. Rev. Lett.* **31**, 972–975.

FLANAGAN, T. B., BIEHL, G. E., CLEWLEY, J. D., RUNDQVIST, S. & ANDERSSON, Y. (1980). *J. Chem. Soc. Faraday Trans.* 1, **76**, 196–208.

FLANAGAN, T. B., BOWERMAN, B. S., RUNDQVIST, S. & ANDERSSON, Y. (1981). To be published.

GULLMAN, L. O. (1966). *J. Less-Common Met.* **11**, 157–167.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.

RUNDQVIST, S. & GULLMAN, L. O. (1960). *Acta Chem. Scand.* **14**, 2246–2247.

SAKATA, M. & COOPER, M. J. (1979). *J. Appl. Cryst.* **12**, 554–563.

THOMAS, J. O. (1977). Report UUIC-B13-9. Institute of Chemistry, Univ. of Uppsala.

Acta Cryst. (1981). B**37**, 1972–1978

Structure of Medaite, $Mn_6[VSi_5O_{18}(OH)]$: The Presence of a New Kind of Heteropolysilicate Anion

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Abstract

A manganese(II) vanadatopentasilicate, medaite $(Mn_{5.774},Ca_{0.190},Fe_{0.035})[(V_{0.815},As_{0.185})Si_5O_{18}(OH)]$, which crystallizes in the monoclinic space group $P2_1/n$, with $a = 6.712$ (1), $b = 28.948$ (8), $c = 7.578$ (2) Å, $\beta = 95.40$ (2)°, $Z = 4$, $V = 1465.9$ Å^3, $D_o = 3.70$ (flotation in Clerici solution), $D_c = 3.727$ Mg m^{-3}, has recently been found in nature as a new mineral. Computer-controlled four-circle diffractometer data (Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, graphite monochromator) were analysed; $F(000) = 1588$, μ(Mo $K\alpha$) = 6.7 mm^{-1}. The final R index = 0.059 for 3350 independent reflections. The structure contains a vanadatopentasilicate anion (with some substitution of As for V) $[VSi_5O_{18}(OH)]^{12-}$, comprising six tetrahedra linked together to form a chain fragment. This ion is another representative of a new series of heteropolysilicate ions, the conformation of which resembles polyphosphates. It can be considered to be an extended relative of a similar ion $[AsSi_3O_{12}(OH)]^{8-}$, recently observed for another new mineral, tiragalloite, which occurs in the same locality.

Introduction

Some interesting new minerals have recently been found in an old manganese mine at Molinello near Chiavari (Liguria), as small orange-yellow to brown grains intimately intergrown with rhodochrosite, quartz, parsettensite, *etc.* (Gramaccioli, Griffin & Mottana, 1979, 1980*a*,*b*). The solution of the crystal structure of one of these minerals showed it to be a

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manganese arsenatotrisilicate, $Mn_4[AsSi_3O_{12}(OH)]$. In this mineral a new kind of 'arsenatotrisilicate' ion $[AsSi_3O_{12}(OH)]^{8-}$ is present, the conformation of which resembles that of a tetrapolyphosphate and can be considered to be an extension of the trisilicate ion (Gramaccioli, Pilati & Liborio, 1979). Therefore, for the first time experimental evidence was obtained on the possibility of finding in nature chain fragments with more than three tetrahedra joined together, filling the gap between trisilicates (very rare) and the much more common silicates with indefinitely long chains.

The presence of such an unusual mineral pointed to unusual physico-chemical conditions of formation, and during the work on mineralogical characterization of this new species, named tiragalloite* (Gramaccioli *et al.*, 1980*a*), attention was drawn to any other accompanying phase. Optical and analytical data were obtained relative to a brown mineral, often intimately associated with tiragalloite, containing essentially Mn, Si, V and some As. After much effort, a small monocrystalline splinter was isolated from the matrix: a preliminary measurement of the unit-cell parameters showed a marked connection with tiragalloite, a, c, and β being almost identical for these two minerals, and the b axis being nearly exactly 1·5 times longer than that for tiragalloite. The possibility of dealing with another representative of this new group of minerals was evident, and an X-ray crystal-structure analysis was considered to be particularly appropriate.

In the meantime, further analytical and optical data were obtained for this new mineral, named medaite (Gramaccioli *et al.*, 1980*b*); the V/As ratio was found to be 0·815/0·185. Since the first fragment showed some satellite reflections which were difficult to suppress, another crystalline splinter was selected which looked more suitable for accurate data collection. This splinter is very irregular in shape, measuring from 0·1 to 0·2 mm in diameter. As for our tiragalloite crystal, in view of the danger of loss, no manipulation of it (*e.g.* grinding it into a sphere) was considered to be advisable.

Determination and refinement of the structure

The crystal was mounted on a Syntex $P\bar{1}$ automatic single-crystal diffractometer. The unit-cell dimensions have been redetermined and refined from 28 reflections, with 2θ around 50°, using Mo $K\alpha$ radiation (λ = 0·71069 Å). The Laue symmetry of the reciprocal lattice is $2/m$, and extinctions are present for $0k0$: $k = 2n + 1$ and $h0l$: $h + l = 2n + 1$. This indicates $P2_1/n$ space-group symmetry.

* The names tiragalloite and medaite for these new minerals have been officially approved by the IMA Commission on New Minerals and Mineral Names.

3350 independent reflections were measured on the Syntex diffractometer, using the 2θ–θ scan method, and Mo $K\alpha$ radiation with a graphite monochromator. These reflections are all those available for 2θ varying between 4·5° and 55°; of these, 200 were too weak, *i.e.* their intensities were less than the corresponding background, brought to the same scale. The reflection intensities were corrected for Lorentz and polarization factors. An empirical absorption correction was also applied modifying the method proposed by Furnas (1957). In our procedure, the empirical Furnas absorption correction $A(hkl) = I_{max}(\varphi)/I_{\varphi(hkl)}$ was rendered dependent upon θ by multiplying it by the absorption correction (μ = 6·7 mm^{-1}) relative to a sphere with diameter equal to 0·1 mm, which is the minimum diameter for the crystal fragment used here. This corresponds to assuming that the value of $I_{max}(\varphi)$, *i.e.* the intensity corresponding to the shortest path within the crystal fragment, is affected by the absorption relative to a sphere, the diameter of which is the smallest possible.

Each reflection was assigned a variance $\sigma^2(I) = \sigma^2_{c.s.}(I) + (0{\cdot}03S)^2$, where $\sigma^2_{c.s.}$ is the variance as derived from counting statistics, and S is the scan count.

From a three-dimensional Patterson synthesis, the positions of all Mn atoms and the V atom were found. A first three-dimensional difference Fourier map obtained by assigning phases consistent with these heavier atoms in the positions derived from the Patterson function showed all the Si and O atoms in the structure. The ideal chemical formula of medaite was found to be $Mn_6[VSi_5O_{18}(OH)]$; the actual composition, derived from the experimental ratios V/As, Mn/Fe and Mn/Ca, as obtained from chemical analysis, is $(Mn_{5\cdot774},Ca_{0\cdot190},Fe_{0\cdot035})[(V_{0\cdot815},As_{0\cdot185})Si_5O_{18}(OH)]$.

Refinement has been carried out by full-matrix least-squares minimization of the quantity $\sum w(|F_o| - |F_c|)^2$. For this purpose, 3150 reflections were considered, *i.e.* all those for which $I > 0$. Final weights were assigned equal to $4|F_o|^2/\sigma^2(|F_o|^2)$; throughout this work, atomic form factors corresponding to the neutral atoms according to Cromer & Waber (1965) have been used, without allowance for the imaginary part of the anomalous dispersion. Similarly, in view of the relatively minor correction ($f' \leq 0{\cdot}4$ for all the heavier atoms present here) even the real part of the anomalous dispersion was not considered.

Owing to the non-negligible substitution by As, the scattering factor of V in this mineral has been taken as a weighted average of the corresponding scattering factors of V and As in the ratio 0·815/0·185, in agreement with the chemical analysis; no refinement of this ratio was attempted on crystallographic grounds. Since only quite minor amounts of Mn are substituted by other elements (Ca and Fe), no allowance has been made for this substitution, and the scattering factor of pure Mn atoms has been used (see also the *Discussion*).

Anisotropic temperature factors were considered for all the atoms in the structure, except the H atom, which was neglected at this stage.

The final R index on the 3150 reflections included in the least squares (for which $I > 0$) is 0·052, and on all the 3350 collected reflections it is 0·059. The final weighted R index is 0·046.* No inconveniences with temperature factors have been observed, all the B's being positive definite; the equivalent B for the (V,As) atom is close to the B's for the Si atoms.

A final difference Fourier synthesis revealed a clear peak of 0·6 e Å^{-3} corresponding to the H atom. This peak lies exactly on the line joining O(1) to O′(19) [the latter related to O(19) by the transformation $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$]. The distance between these two atoms (2·788 Å) is well within the range for a typical O···H–O hydrogen bond, and the O(1)–H bond is 0·98 Å long.

Besides the peak corresponding to the H atom, other positive and negative peaks (up to 1·1 e Å^{-3}) appear in the final difference map, close to the heavier atoms. Such a situation is probably connected with partial inadequacy of atomic form factors, especially in view of the imaginary contribution in anomalous scattering being neglected. The final positional parameters are given in Table 1.

The standard deviation in the X–O (X = Mn, Si, V) bond lengths, as derived from the residuals and the normal-equation matrix in the final least-squares cycle, is around 0·004 Å; for the O–X–O and X–O–X bond angles it is around 0·15°. Bond lengths and angles are reported in Fig. 1, and Tables 2 and 3.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36148 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent or isotropic thermal parameters with e.s.d.'s in parentheses*

	x	y	z	B_{eq} (Å^2)
V	0·4926 (1)	0·21363 (3)	0·8804 (1)	0·88 (2)
Si(1)	0·6940 (2)	0·16672 (5)	0·5892 (2)	0·88 (4)
Si(2)	0·6415 (2)	0·06220 (5)	0·5159 (2)	0·80 (4)
Si(3)	0·8652 (2)	0·01208 (5)	0·2289 (2)	0·86 (4)
Si(4)	0·8158 (2)	−0·09403 (5)	0·1653 (2)	0·83 (4)
Si(5)	1·0371 (2)	−0·14571 (5)	−0·1141 (2)	0·84 (4)
O(1)	0·6544 (6)	0·25772 (13)	0·8557 (5)	1·05 (12)
O(2)	0·4569 (6)	0·20238 (13)	1·0889 (5)	1·09 (12)
O(3)	0·2796 (6)	0·22463 (14)	0·7593 (5)	1·17 (12)
O(4)	0·6062 (6)	0·16425 (13)	0·7890 (5)	1·06 (12)
O(5)	0·5124 (6)	0·18469 (13)	0·4500 (5)	1·08 (12)
O(6)	0·8896 (6)	0·19857 (13)	0·6003 (5)	0·91 (11)
O(7)	0·7529 (6)	0·11262 (13)	0·5523 (5)	1·07 (12)
O(8)	0·4475 (6)	0·06913 (13)	0·3759 (5)	1·03 (11)
O(9)	0·5989 (6)	0·04201 (13)	0·7042 (5)	0·95 (11)
O(10)	0·8053 (6)	0·03026 (13)	0·4235 (5)	1·05 (12)
O(11)	1·0747 (6)	0·03697 (13)	0·2093 (5)	1·00 (12)
O(12)	0·6854 (6)	0·02299 (13)	0·0754 (5)	0·87 (11)
O(13)	0·8978 (6)	−0·04393 (13)	0·2448 (5)	0·95 (11)
O(14)	0·6306 (6)	−0·09027 (13)	0·0132 (5)	0·86 (11)
O(15)	0·7787 (6)	−0·12081 (13)	0·3443 (5)	1·04 (12)
O(16)	1·0031 (6)	−0·11675 (13)	0·0684 (5)	0·91 (11)
O(17)	1·2526 (6)	−0·12771 (13)	−0·1532 (5)	1·01 (11)
O(18)	0·8647 (6)	−0·13917 (13)	−0·2766 (5)	0·90 (11)
O(19)	1·0326 (7)	−0·20096 (13)	−0·0516 (5)	1·30 (12)
Mn(1)	0·3700 (1)	0·02239 (3)	0·1546 (1)	0·67 (2)
Mn(2)	0·6808 (1)	0·31736 (3)	0·0237 (1)	0·69 (2)
Mn(3)	0·4556 (1)	0·13625 (3)	0·2214 (1)	0·67 (2)
Mn(4)	0·6687 (1)	0·08683 (3)	0·9182 (1)	0·75 (2)
Mn(5)	0·1412 (1)	0·07642 (3)	0·4413 (1)	0·94 (2)
Mn(6)	0·4742 (1)	0·25294 (3)	0·3087 (1)	0·83 (2)
(H	0·967	−0·215	−0·159)	

Discussion

The most interesting structural characteristic of medaite is the presence of the vanadatopentasilicate ion $[VSi_5O_{18}(OH)]^{12-}$. This ion is not related to anything known, except the arsenatotrisilicate ion $[AsSi_3O_{12}(OH)]^{8-}$ found in tiragalloite. The resemblance is indeed striking on comparing Fig. 1 of this work with the corresponding Fig. 1 of our previous work on tiragalloite (Gramaccioli, Pilati & Liborio, 1979): the conformation of the vanadatopentasilicate ion can be almost exactly derived from the corresponding

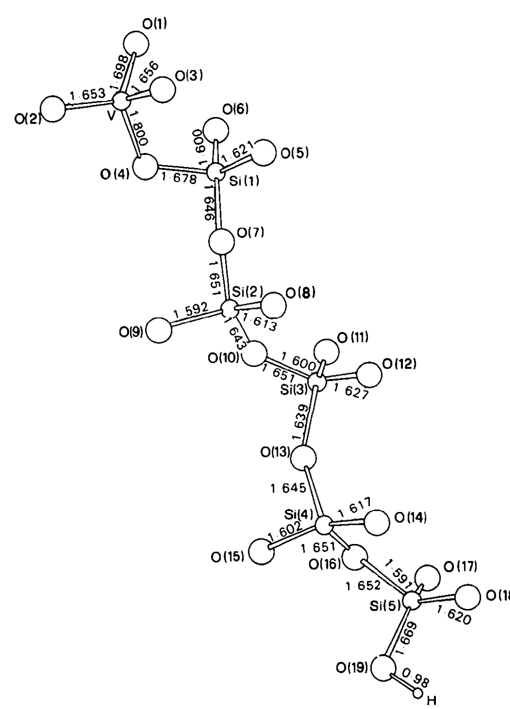

Fig. 1. Conformation of the $[VSi_5O_{18}(OH)]^{12-}$ ion.

Table 2. *Bond angles (°) in the anion*

O(1)–V–O(2)	113·9	O(1)–V–O(3)	108·8
O(1)–V–O(4)	104·9	O(2)–V–O(3)	111·9
O(2)–V–O(4)	108·5	O(3)–V–O(4)	108·4
O(4)–Si(1)–O(5)	107·1	O(4)–Si(1)–O(6)	109·5
O(4)–Si(1)–O(7)	102·9	O(5)–Si(1)–O(6)	114·4
O(5)–Si(1)–O(7)	111·9	O(6)–Si(1)–O(7)	110·4
O(7)–Si(2)–O(8)	108·9	O(7)–Si(2)–O(9)	107·0
O(7)–Si(2)–O(10)	105·0	O(8)–Si(2)–O(9)	115·6
O(8)–Si(2)–O(10)	108·7	O(9)–Si(2)–O(10)	111·0
O(10)–Si(3)–O(11)	103·3	O(10)–Si(3)–O(12)	110·5
O(10)–Si(3)–O(13)	107·0	O(11)–Si(3)–O(12)	116·5
O(11)–Si(3)–O(13)	109·9	O(12)–Si(3)–O(13)	109·2
O(13)–Si(4)–O(14)	114·2	O(13)–Si(4)–O(15)	101·0
O(13)–Si(4)–O(16)	105·7	O(14)–Si(4)–O(15)	117·8
O(14)–Si(4)–O(16)	106·0	O(15)–Si(4)–O(16)	111·7
O(16)–Si(5)–O(17)	100·9	O(16)–Si(5)–O(18)	115·6
O(16)–Si(5)–O(19)	104·0	O(17)–Si(5)–O(18)	114·7
O(17)–Si(5)–O(19)	114·1	O(18)–Si(5)–O(19)	107·3
V–O(4)–Si(1)	120·9	Si(1)–O(7)–Si(2)	139·2
Si(2)–O(10)–Si(3)	142·1	Si(3)–O(13)–Si(4)	143·9
Si(4)–O(16)–Si(5)	138·2		

arsenatotrisilicate, by repeating twice the last two tetrahedra centred on Si atoms (opposite to the As atom). In view of this analogy, and of the similarity between As—O and V—O bonds, the partial substitution of the V atom by As is not surprising; a limited substitution of the As atom by V in tiragalloite has also been detected (Gramaccioli *et al.*, 1980*a*), and the two minerals occur in close association with each other.

This vanadatopentasilicate ion gives further practical evidence for considerably long, unbranched polynuclear ions intermediate between $(X_2O_7)^{n-}$, which are well represented in nature by several common silicates, and indefinite $(XO_3)^{m-}_{\infty}$ chains, which are also well represented in nature by the so-called *ino*-silicates. The existence of such an ion, comprising six tetrahedra, substantially extends the field of the so-called *soro*-silicates, which have been defined as a series of compounds having terminated groups of SiO_4 tetrahedra: see, for instance, Strunz (1977). The packing of the vanadatopentasilicate chains is shown in Fig. 2.

In the vanadatopentasilicate ion, the average of the Si—O bond lengths (1·630 Å) is in good agreement with the average (1·623 Å) reported by Smith & Bailey (1963) for metasilicates with no substitution of Al for Si. The average of the V—O bond lengths (1·702 Å) is somewhat less than the average (1·74 Å) reported by Ondik & Smith (1962) for orthovanadates, or than the average (1·735 Å) of the bond lengths reported by the same authors for terminal (1·66 Å) or bridged (1·81 Å) V—O bonds in vanadates with tetrahedral coordination around the metal. If we assume the average of As—O bond lengths to be 1·693 Å, following Ferraris (1970), a partial substitution of V by As necessarily implies some shortening with respect to the 'pure' V—O bond lengths: the average of the corresponding data reported

Table 3. *Bond distances (Å) and angles (°) around the* Mn *atoms*

Mn(1)–O(8)[a]	2·179	Mn(1)–O(9)[b]	2·150
Mn(1)–O(11)[c]	2·105	Mn(1)–O(12)[a]	2·254
Mn(1)–O′(12)[d]	2·187	Mn(1)–O(14)[d]	2·341
Average Mn(1)–O	2·203		
O(8)–Mn(1)–O(9)	98·6	O(8)–Mn(1)–O(11)	83·4
O(8)–Mn(1)–O(12)	92·2	O(8)–Mn(1)–O′(12)	175·4
O(8)–Mn(1)–O(14)	83·4	O(9)–Mn(1)–O(11)	97·2
O(9)–Mn(1)–O(12)	95·1	O(9)–Mn(1)–O′(12)	82·9
O(9)–Mn(1)–O(14)	173·5	O(11)–Mn(1)–O(12)	167·4
O(11)–Mn(1)–O′(12)	100·7	O(11)–Mn(1)–O(14)	89·2
O(12)–Mn(1)–O′(12)	83·4	O(12)–Mn(1)–O(14)	78·6
O′(12)–Mn(1)–O(14)	94·6		
Mn(2)–O(1)[e]	2·143	Mn(2)–O(3)[f]	2·209
Mn(2)–O(6)[f]	2·346	Mn(2)–O(6)[g]	2·141
Mn(2)–O(15)[h]	2·056	Mn(2)–O(18)[k]	2·253
Average Mn(2)–O	2·191		
O(1)–Mn(2)–O(3)	92·2	O(1)–Mn(2)–O(5)	82·3
O(1)–Mn(2)–O(6)	87·8	O(1)–Mn(2)–O(15)	172·0
O(1)–Mn(2)–O(18)	87·6	O(3)–Mn(2)–O(5)	87·7
O(3)–Mn(2)–O(6)	82·8	O(3)–Mn(2)–O(15)	94·0
O(3)–Mn(2)–O(18)	170·3	O(5)–Mn(2)–O(6)	165·9
O(5)–Mn(2)–O(15)	93·0	O(5)–Mn(2)–O(18)	82·7
O(6)–Mn(2)–O(15)	97·9	O(6)–Mn(2)–O(18)	106·9
O(15)–Mn(2)–O(18)	85·4		
Mn(3)–O(2)[e]	2·162	Mn(3)–O(5)[a]	2·233
Mn(3)–O(8)[a]	2·272	Mn(3)–O(14)[d]	2·253
Mn(3)–O(17)[l]	2·086	Mn(3)–O(18)[d]	2·230
Average Mn(3)–O	2·206		
O(2)–Mn(3)–O(5)	78·3	O(2)–Mn(3)–O(8)	176·3
O(2)–Mn(3)–O(14)	99·7	O(2)–Mn(3)–O(17)	86·8
O(2)–Mn(3)–O(18)	95·7	O(5)–Mn(3)–O(8)	98·5
O(5)–Mn(3)–O(14)	174·6	O(5)–Mn(3)–O(17)	99·8
O(5)–Mn(3)–O(18)	85·9	O(8)–Mn(3)–O(14)	83·4
O(8)–Mn(3)–O(17)	95·5	O(8)–Mn(3)–O(18)	82·3
O(14)–Mn(3)–O(17)	84·9	O(14)–Mn(3)–O(18)	89·4
O(17)–Mn(3)–O(18)	174·1		
Mn(4)–O(4)[a]	2·466	Mn(4)–O(7)[a]	2·976
Mn(4)–O(9)[a]	2·095	Mn(4)–O(12)[m]	2·196
Mn(4)–O(14)[b]	2·124	Mn(4)–O(16)[n]	2·360
Mn(4)–O(17)[n]	2·162		
Average Mn(4)–O	2·340		
Average of the 4 shortest bonds	2·144		
O(4)–Mn(4)–O(7)	56·1	O(4)–Mn(4)–O(9)	103·8
O(4)–Mn(4)–O(12)	168·1	O(4)–Mn(4)–O(14)	85·7
O(4)–Mn(4)–O(16)	78·9	O(4)–Mn(4)–O(17)	81·3
O(7)–Mn(4)–O(9)	58·8	O(7)–Mn(4)–O(12)	135·4
O(7)–Mn(4)–O(14)	118·9	O(7)–Mn(4)–O(16)	71·9
O(7)–Mn(4)–O(17)	85·3	O(9)–Mn(4)–O(12)	84·0
O(9)–Mn(4)–O(14)	94·1	O(9)–Mn(4)–O(16)	113·6
O(9)–Mn(4)–O(17)	174·9	O(12)–Mn(4)–O(14)	84·7
O(12)–Mn(4)–O(16)	106·6	O(12)–Mn(4)–O(17)	91·0
O(14)–Mn(4)–O(16)	150·8	O(14)–Mn(4)–O(17)	86·3
O(16)–Mn(4)–O(17)	67·0		
Mn(5)–O(7)[c]	3·002	Mn(5)–O(8)[a]	2·170
Mn(5)–O(10)[c]	2·613	Mn(5)–O(11)[c]	2·109
Mn(5)–O(13)[b]	2·594	Mn(5)–O(15)[b]	2·101
Mn(5)–O(18)[d]	2·202		
Average Mn(5)–O	2·399		
Average of the 4 shortest bonds	2·146		

Table 3 (*cont.*)

O(7)–Mn(5)–O(8)	164·6	O(7)–Mn(5)–O(10)	54·9
O(7)–Mn(5)–O(11)	107·6	O(7)–Mn(5)–O(13)	72·8
O(7)–Mn(5)–O(15)	74·7	O(7)–Mn(5)–O(18)	84·3
O(8)–Mn(5)–O(10)	140·3	O(8)–Mn(5)–O(11)	83·6
O(8)–Mn(5)–O(13)	110·7	O(8)–Mn(5)–O(15)	93·3
O(8)–Mn(5)–O(18)	85·3	O(10)–Mn(5)–O(11)	64·3
O(10)–Mn(5)–O(13)	72·6	O(10)–Mn(5)–O(15)	120·6
O(10)–Mn(5)–O(18)	115·0	O(11)–Mn(5)–O(13)	122·5
O(11)–Mn(5)–O(15)	174·0	O(11)–Mn(5)–O(18)	89·0
O(13)–Mn(5)–O(15)	63·5	O(13)–Mn(5)–O(18)	145·2
O(15)–Mn(5)–O(18)	85·6		
$Mn(6)–O(1)^{(g)}$	2·230	$Mn(6)–O(2)^{(m)}$	2·213
$Mn(6)–O(3)^{(f)}$	2·215	$Mn(6)–O(5)^{(a)}$	2·250
$Mn(6)–O(6)^{(g)}$	2·149	$Mn(6)–O(19)^{(h)}$	2·277
Average Mn(6)–O		2·222	
O(1)–Mn(6)–O(2)	92·6	O(1)–Mn(6)–O(3)	170·9
O(1)–Mn(6)–O(5)	82·6	O(1)–Mn(6)–O(6)	90·9
O(1)–Mn(6)–O(19)	81·9	O(2)–Mn(6)–O(3)	92·9
O(2)–Mn(6)–O(5)	76·9	O(2)–Mn(6)–O(6)	83·5
O(2)–Mn(6)–O(19)	173·0	O(3)–Mn(6)–O(5)	105·8
O(3)–Mn(6)–O(6)	82·5	O(3)–Mn(6)–O(19)	93·1
O(5)–Mn(6)–O(6)	159·0	O(5)–Mn(6)–O(19)	98·1
O(6)–Mn(6)–O(19)	100·8		

Symmetry transformations: (*a*) x,y,z; (*b*) $1-x, -y, 1-z$; (*c*) $x-1, y, z$; (*d*) $1-x, -y, -z$; (*e*) $x, y, z-1$; (*f*) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$; (*g*) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (*h*) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (*k*) $\frac{3}{2}-x, \frac{1}{2}+y, -z-\frac{1}{2}$; (*l*) $2-x, -y, -z$; (*m*) $x, y, 1+z$; (*n*) $2-x, -y, 1-z$.

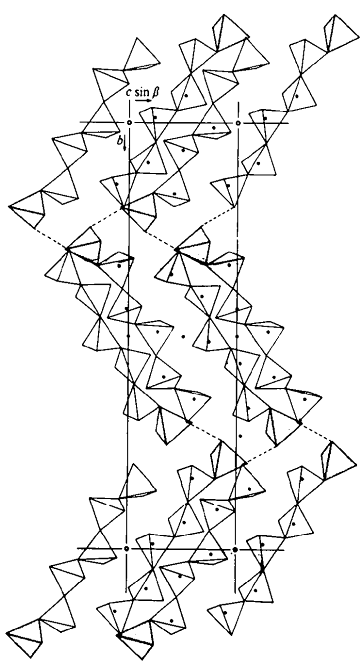

Fig. 2. Packing of the vanadatopentasilicate chain fragment in the crystal, as seen along **a**. The Mn (and Si) atoms have been indicated by points; shaded tetrahedra correspond to VO_4. Hydrogen bonds are shown as dashed lines.

in the literature, weighted according to the results of chemical analysis, gives 1·72 Å.

As in the arsenatotrisilicate ion of tiragalloite, and like the di- and trisilicates, pyro- or diphosphates *etc.*, the 'bridged' Si–O (or V–O) bonds are distinctly longer than the others, in agreement with the theoretical results obtained by Cruickshank (1961) and other authors (Louisnathan & Gibbs, 1972*a*,*b*; Tossell & Gibbs, 1976). Here, for instance, the 'bridged' Si–O bond-length average is 1·651 Å, whereas the 'non-bridged' Si–O bond-length average is 1·608 Å, two values which are close to the corresponding averages (1·652 and 1·602 Å respectively) found for the arsenatotrisilicate ion in tiragalloite (Gramaccioli, Pilati & Liborio, 1979), or to 1·656 and 1·603 Å respectively, found for the trisilicate ion in rosenhahnite (Wan, Ghose & Gibbs, 1977).

For other examples of the trisilicate ion, the difference between 'bridged' and 'non-bridged' Si–O bond lengths seems to be somewhat smaller: for instance, the corresponding averages are 1·648 and 1·626 Å respectively, in ardennite (Donnay & Allmann, 1968), or 1·634 and 1·617 Å respectively, in kinoite (Laughon, 1971). The Si–OH bond (1·669 Å) is considerably longer here than the Si–O bonds, as is usual; for tiragalloite and rosenhahnite the corresponding values are 1·669 and 1·662 Å respectively (for the latter case, the reported value is the average of two different bonds).

It must be pointed out that all these values are not corrected for thermal libration; for this reason, they are liable to some modification, albeit not a substantial one, in view of the relatively low values of the temperature factors compared with molecular crystals.

The variation in bond lengths can also be described in terms of Pauling bond strength (see, for instance, Baur, 1970). For this purpose, estimated bond strengths according to Brown & Wu (1976), and their sum with respect to each O atom are reported in Table 4.

Oxygen–metal distances below 3·01 Å around the Mn atoms are given in Table 3. For Mn(1), Mn(2), Mn(3) and Mn(6), the O atoms are almost octahedrally arranged around the metal, with relatively little distortion: the bond lengths range between 2·056 and 2·341 Å, their average being 2·205 Å, with little variation between the three polyhedra. This is in good agreement with the average Mn^{2+}–O distance (2·22 Å) reported by Shannon & Prewitt (1969), with the corresponding average in tiragalloite (2·222 Å), and with several well refined crystal structures of Mn^{2+} compounds. Fig. 3 illustrates the coordination polyhedra around the Mn atoms.

For two Mn atoms, *i.e.* Mn(4) and Mn(5), the situation is more irregular. For these atoms, the coordination number is seven (4 + 2 + 1): there are, in fact, four shorter Mn–O bonds ranging from 2·095 to 2·202 Å, two medium–long bonds ranging from 2·360

Table 4. *Estimated Pauling bond strengths* s_l

Here, the coefficients of Brown & Wu (1976) have been used, thereby relating the s_l's to bond lengths.

'Anions'	'Cations'	s_l	$\sum s_l$
O(1)	Mn(2)	0·37	1·98
	Mn(6)	0·30	
	V	1·31	
O(2)	Mn(3)	0·36	2·18
	Mn(6)	0·31	
	V	1·51	
O(3)	Mn(2)	0·32	2·12
	Mn(6)	0·31	
	V	1·49	
O(4)	Mn(4)	0·17	2·00
	V	0·97	
	Si(1)	0·86	
O(5)	Mn(2)	0·23	1·81
	Mn(3)	0·30	
	Mn(6)	0·28	
	Si(1)	1·00	
O(6)	Mn(2)	0·38	1·81
	Mn(6)	0·37	
	Si(1)	1·06	
O(7)	Mn(4)	0·06	1·99
	Mn(5)	0·06	
	Si(1)	0·94	
	Si(2)	0·93	
O(8)	Mn(1)	0·34	1·98
	Mn(3)	0·27	
	Mn(5)	0·35	
	Si(2)	1·02	
O(9)	Mn(1)	0·37	1·87
	Mn(4)	0·42	
	Si(2)	1·08	
O(10)	Mn(5)	0·12	2·00
	Si(2)	0·95	
	Si(3)	0·93	
O(11)	Mn(1)	0·41	1·88
	Mn(5)	0·41	
	Si(3)	1·06	
O(12)	Mn(1)	0·28	1·91
	Mn(1')	0·33	
	Mn(4)	0·33	
	Si(3)	0·97	
O(13)	Mn(5)	0·13	2·03
	Si(3)	0·96	
	Si(4)	0·94	
O(14)	Mn(1)	0·23	1·91
	Mn(3)	0·28	
	Mn(4)	0·39	
	Si(4)	1·01	
O(15)	Mn(2)	0·47	1·94
	Mn(5)	0·42	
	Si(4)	1·05	
O(16)	Mn(4)	0·22	2·07
	Si(4)	0·93	
	Si(5)	0·92	
O(17)	Mn(3)	0·44	1·88
	Mn(4)	0·36	
	Si(5)	1·08	
O(18)	Mn(2)	0·28	1·90
	Mn(3)	0·30	
	Mn(5)	0·32	
	Si(5)	1·00	
O(19)	Mn(6)	0·27	1·92
	Si(5)	0·88	
	H	0·77	

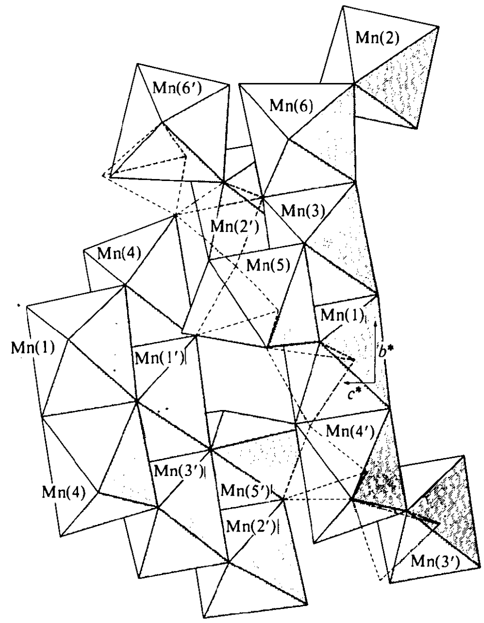

Fig. 3. Coordination polyhedra around Mn atoms, as seen along **a** [the longest distances around Mn(4) and Mn(5) are not shown]. A vanadatopentasilicate chain fragment (dashed tetrahedra) is superimposed.

to 2·613 Å, and one long bond nearly exactly 3 Å [2·976 and 3·002 Å for Mn(4)–O(7) and Mn(5)–O(7) respectively]. This situation is similar to that found for one Mn atom in tiragalloite [there named Mn(4)]; in our former work (Gramaccioli, Pilati & Liborio, 1979), we had described it as '5 + 2', but it could also (and probably more correctly) be considered as '4 + 2 + 1'. However, there is a difference; in tiragalloite for the same atom [Mn(4)] the 'medium–long' bonds are 2·366 and 2·625 Å, whereas in medaite the 2·40 and 2·60 Å bonds are relative to *different* Mn atoms (see Table 3).

Since the chemical analysis has revealed the presence of a little Ca, it is possible for this metal to prefer the Mn^{2+} sites with a higher coordination number, because the ionic radius of Ca^{2+} is appreciably greater than that of Mn^{2+} (0·99 and 0·80 Å respectively, according to Ahrens, 1952). This effect can be noticed, for instance, in ardennite (Donnay & Allmann, 1968) and in other calciferous Mn^{2+} silicates; in our case, the equivalent *B* of Mn(5), which is higher than for any other Mn atom, and whose Mn—O bonds are, on the whole, the longest ones, might reflect some partial substitution by lighter atoms.

However, just because the Mn—O bonds are long and therefore weaker than the average, there is no reason why the *real B* should not be higher than that for the other atoms. Moreover, in view of the very limited substitution in medaite, the possible effects of absorption, and the lack of any theoretical estimate for the partition coefficient of Ca^{2+} between the various sites, and since neither a realistic guess of the temperature of formation of this mineral, nor precise packing-energy calculations have been made, it is beyond the scope and the accuracy of the present work to take this possibility into account.

The constant interest and encouragement given to this work by Professor Giuseppe Schiavinato is gratefully acknowledged.

References

AHRENS, L. H. (1952). *Geochim. Cosmochim. Acta*, **2**, 155–169.
BAUR, W. H. (1970). *Trans. Am. Crystallogr. Assoc.* **6**, 129–155.
BROWN, I. D. & WU, K. K. (1976). *Acta Cryst.* B**32**, 1957–1959.
CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
CRUICKSHANK, D. W. J. (1961). *J. Chem. Soc.* pp. 5486–5504.
DONNAY, G. & ALLMANN, R. (1968). *Acta Cryst.* B**24**, 845–855.
FERRARIS, G. (1970). *Rend. Soc. Ital. Mineral. Petrol.* **26**, 589–598.
FURNAS, T. C. (1957). *Single Crystal Orienter Instruction Manual*. Milwaukee: General Electric Company.
GRAMACCIOLI, C. M., GRIFFIN, W. L. & MOTTANA, A. (1979). *Rend. Soc. Ital. Mineral. Petrol.* **35**, 145–149.
GRAMACCIOLI, C. M., GRIFFIN, W. L. & MOTTANA, A. (1980*a*). *Am. Mineral.* **65**, 947–952.
GRAMACCIOLI, C. M., GRIFFIN, W. L. & MOTTANA, A. (1980*b*). *Rend. Soc. Ital. Mineral. Petrol.* **36**, 159–163.
GRAMACCIOLI, C. M., PILATI, T. & LIBORIO, G. (1979). *Acta Cryst.* B**35**, 2287–2291.
LAUGHON, R. B. (1971). *Am. Mineral.* **56**, 193–200.
LOUISNATHAN, S. J. & GIBBS, G. V. (1972*a*). *Am. Mineral.* **57**, 1614–1642.
LOUISNATHAN, S. J. & GIBBS, G. V. (1972*b*). *Am. Mineral.* **57**, 1643–1663.
ONDIK, H. & SMITH, D. (1962). *International Tables for X-ray Crystallography*, Vol. III, pp. 257–274. Birmingham: Kynoch Press.
SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* B**25**, 925–946.
SMITH, J. V. & BAILEY, S. W. (1963). *Acta Cryst.* **16**, 801–811.
STRUNZ, H. (1977). *Mineralogische Tabellen*, 6th ed. Leipzig: Geest & Portig.
TOSSELL, J. A. & GIBBS, G. V. (1976). *Am. Mineral.* **61**, 287–294.
WAN, C., GHOSE, S. & GIBBS, G. V. (1977). *Am. Mineral.* **62**, 503–512.

Acta Cryst. (1981). B**37**, 1978–1982

Structure de Sulfate de Vanadyle–Acide Sulfurique (2:1)

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Abstract

The structure of $2VOSO_4.H_2SO_4$ has been determined by single-crystal X-ray techniques. The compound crystallizes in the tetragonal system, space group $P4_2/mnm$, with cell parameters $a = 8{\cdot}971$ (3), $c = 15{\cdot}594$ (2) Å, $Z = 4$, $V = 1254{\cdot}99$ Å^3, $d_m = 2{\cdot}18$, $d_x = 2{\cdot}24$ Mg m^{-3}. $R = 0{\cdot}077$ for 340 independent reflexions. VO_6 octahedra are linked by monodentate SO_4 tetrahedra to form polymeric $[VOSO_4]_\infty$ layers which are joined together by sulphuric acid molecules. Ladwig's hypothesis [Ladwig (1969), *Z. Anorg. Allg. Chem.* **364**, 225–240] concerning α-$VOSO_4.H_2O$ is confirmed. He suggested an ordered insertion of the water molecules between the layers.

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Introduction

Lorsqu'on chauffe à 363 K une solution d'acide sulfurique concentrée (contenant 80% d'acide sulfuri-