

## Structure of Sodium $\beta$ -Hydrogenenneatungstosilicate Hydrate $\text{Na}_9(\beta\text{-SiW}_9\text{O}_{34}\text{H}) \cdot 23\text{H}_2\text{O}$

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### Abstract

$\text{Na}_9(\beta\text{-SiW}_9\text{O}_{34}\text{H}) \cdot 23\text{H}_2\text{O}$  is triclinic with  $a = 13.166$  (3),  $b = 12.609$  (3),  $c = 18.350$  (4) Å,  $\alpha = 69.53$  (3),  $\beta = 73.51$  (4),  $\gamma = 63.16$  (3)°,  $Z = 2$ , space group  $P\bar{1}$ . The final  $R = 0.059$  for 4596 non-zero diffractometer reflexions. Results are discussed with regard both to the connexion between chemical behaviour and isomerism and to the  $\text{Na}^+$  cations in the crystalline state.

### Introduction

The  $\beta$ -enneatungstosilicate is the first species which can be obtained by acidification of a mixture of tungstate and silicate. By addition of tungstate and acidification it gives in a first step the  $\beta_1$ -undecatungstosilicate and in a second step the  $\beta$ -dodecatungstosilicate. The structures of these compounds are known (Robert, Tézé, Hervé & Jeannin, 1980; Matsumoto, Kobayashi & Sasaki, 1975). We think that no major structural change occurs in these very fast reactions. Vibration spectroscopy supports this hypothesis. The spectra of the anions  $\alpha\text{-SiW}_{12}\text{O}_{40}^{4-}$ ,  $\alpha\text{-SiW}_{11}\text{O}_{39}^{3-}$  and  $\alpha\text{-SiW}_9\text{O}_{34}^{10-}$  show the same general features with, however, in the stretching region, a significant frequency decrease (Rocchiccioli-Deltcheff, Thouvenot & Franck, 1976).

Two structural patterns denoted *A* and *B* have been proposed for enneapolyanions (Hervé & Tézé, 1977) but no chemical argument provides real evidence for one or the other geometry and, therefore, a structural determination was necessary.

### Experimental

The solution of the structure was performed on crystals of  $\beta\text{-Na}_9\text{SiW}_9\text{O}_{34}\text{H} \cdot 23\text{H}_2\text{O}$  prepared according to Hervé & Tézé (1977).

The crystals are colourless pellucid plates. Cell dimensions and the space group were obtained from oscillation and Weissenberg photographs. They

revealed no symmetry and the space group was either  $P1$  or  $P\bar{1}$ . The cell dimensions were refined by least squares from the settings of 19 homogeneously distributed reflexions which were measured on a three-circle diffractometer. The cell dimensions are given in the *Abstract*. The density calculated for  $Z = 2$  ( $D_c = 3.757$ ) agrees with that measured by pycnometry ( $D_m = 3.55 \text{ Mg m}^{-3}$ ).

For data collection a crystal  $0.04 \times 0.04 \times 0.02$  mm was mounted on a CAD-3 Enraf–Nonius diffractometer with *a* parallel to the  $\varphi$  axis of the diffractometer; 8950 independent reflexions were measured in the  $\theta$ – $2\theta$  scan mode up to  $2\theta = 50^\circ$  with Zr-filtered Mo *K* $\alpha$  [ $\lambda(\text{Mo } K\alpha) = 0.71069$  Å] radiation. The scan width varied according to  $\Delta\theta$  (°) =  $0.7 + 0.34 \text{ tg } \theta$ . Two standard reflexions were monitored every 50 reflexions and remained constant.  $\sigma(I)$  calculated according to counting statistics allowed us to consider 4596 reflexions with  $I > 2.5 \sigma(I)$  as observed. The other reflexions were omitted from further calculations. The intensities were corrected for Lorentz and polarization factors. A Wilson plot gave the overall temperature factor ( $B = 0.77 \text{ \AA}^2$ ) and the scale factor. Absorption corrections ( $\mu = 21.14 \text{ mm}^{-1}$ ) were applied (Wehe, Busing & Levy, 1962). A statistical test with the normalized structure factors unambiguously showed the space group to be  $P\bar{1}$ .

The structure was solved by the heavy-atom method. A Patterson synthesis revealed only three peaks corresponding to the three main  $\text{W} \cdots \text{W}$  vectors. These peaks are multiple because of the symmetry of the polyanion. We had therefore several solutions to try. Attempts were carried out assuming that the polyanion was a 12-tungstosilicate (Keggin structure). Among the 12 W atoms introduced in a least-squares refinement, three with increasing *B* values were considered as erroneous. The nine remaining W atoms were kept. Successive difference syntheses and full-matrix least-squares cycles led to the whole polyanionic structure. At this stage *R* was 0.098 with anisotropic thermal parameters for W and Si. The  $\text{Na}^+$  ions and water molecules were located and refined isotropically with

Table 1. Fractional atomic coordinates ( $\times 10^5$  for W and  $\times 10^4$  for other atoms) and isotropic thermal parameters

For W and Si atoms $B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$				
	x	y	z	$B_{\text{eq}}/B$ ( $\text{\AA}^2$ )
W(1)	36821 (11)	14437 (12)	20823 (7)	1.23 (10)
W(2)	21397 (12)	11066 (14)	10267 (7)	1.71 (11)
W(3)	10969 (12)	36988 (12)	16297 (9)	1.78 (11)
W(4)	27711 (11)	9712 (12)	42633 (7)	1.09 (9)
W(5)	38177 (11)	-14990 (12)	35991 (7)	1.11 (10)
W(6)	20453 (11)	-18432 (12)	25022 (8)	1.31 (10)
W(7)	-4614 (11)	3837 (12)	21317 (7)	1.17 (10)
W(8)	-15811 (11)	32187 (12)	28157 (7)	1.21 (10)
W(9)	-910 (11)	34776 (12)	38621 (8)	1.29 (10)
Si	1194 (7)	920 (8)	3036 (5)	1.3 (7)
O <sub>a</sub> (123)	1823 (19)	1581 (20)	2235 (13)	1.4 (4)
O <sub>a</sub> (45)	2109 (17)	199 (18)	3665 (11)	0.8 (3)
O <sub>a</sub> (67)	849 (17)	-49 (18)	2856 (11)	0.8 (3)
O <sub>a</sub> (89)	34 (17)	1994 (18)	3371 (11)	0.8 (3)
O <sub>b</sub> (14)	3280 (21)	1721 (23)	3059 (15)	2.1 (4)
O <sub>b</sub> (15)	4068 (18)	-269 (19)	2559 (12)	1.3 (4)
O <sub>b</sub> (26)	2620 (20)	-528 (21)	1610 (14)	1.7 (4)
O <sub>b</sub> (27)	652 (19)	1182 (21)	1284 (13)	1.5 (4)
O <sub>b</sub> (38)	-346 (19)	3643 (21)	1904 (13)	1.5 (4)
O <sub>b</sub> (39)	918 (19)	3869 (21)	2683 (13)	1.6 (4)
O <sub>b</sub> (49)	1386 (18)	2401 (19)	4083 (12)	1.0 (3)
O <sub>b</sub> (56)	3138 (19)	-1866 (21)	3000 (13)	1.6 (4)
O <sub>b</sub> (78)	-1175 (20)	1936 (22)	2341 (14)	1.8 (4)
O <sub>c</sub> (12)	3526 (18)	1173 (20)	1148 (13)	1.3 (4)
O <sub>c</sub> (13)	2771 (21)	3139 (22)	1616 (14)	1.9 (4)
O <sub>c</sub> (23)	1505 (22)	2928 (23)	773 (15)	2.2 (4)
O <sub>c</sub> (45)	4080 (21)	-455 (22)	4047 (14)	1.9 (4)
O <sub>c</sub> (67)	788 (19)	-1082 (21)	1902 (13)	1.5 (4)
O <sub>c</sub> (89)	-1335 (18)	4247 (19)	3251 (12)	0.9 (3)
O <sub>d</sub> (1)	5046 (20)	1535 (22)	1756 (14)	1.8 (4)
O <sub>d</sub> (2)	2501 (21)	1020 (22)	52 (14)	2.0 (4)
O <sub>d</sub> (3)	826 (21)	5181 (23)	1044 (14)	2.1 (4)
O <sub>d</sub> (4)	3509 (20)	1599 (22)	4546 (14)	1.8 (4)
O <sub>d</sub> (4)'	2246 (19)	203 (21)	5181 (13)	1.6 (4)
O <sub>d</sub> (5)	5224 (19)	-2511 (21)	3457 (13)	1.6 (4)
O <sub>d</sub> (5)'	3339 (21)	-2309 (23)	4495 (15)	2.0 (4)
O <sub>d</sub> (6)	2884 (19)	-2998 (20)	2038 (13)	1.5 (4)
O <sub>d</sub> (6)'	1330 (21)	-2591 (22)	3352 (14)	1.8 (4)
O <sub>d</sub> (7)	-1228 (22)	714 (24)	1387 (15)	2.4 (5)
O <sub>d</sub> (7)'	-1189 (19)	-354 (21)	2977 (13)	1.5 (4)
O <sub>d</sub> (8)	-2681 (23)	4348 (25)	2290 (16)	2.6 (5)
O <sub>d</sub> (8)'	-2387 (19)	2642 (20)	3694 (13)	1.5 (4)
O <sub>d</sub> (9)	-135 (25)	4826 (27)	3992 (17)	3.1 (5)
O <sub>d</sub> (9)'	-797 (21)	2869 (22)	4743 (14)	1.9 (4)
Na(1)	-2463 (13)	-2068 (14)	1306 (9)	2.5 (3)
Na(2)	-2048 (13)	-1759 (14)	3053 (9)	2.3 (3)
Na(3)	-2962 (13)	1026(14)	3612 (9)	2.6 (3)
Na(4)	-333 (14)	-1475 (15)	4155 (10)	3.0 (3)
Na(5)	-40 (17)	1328 (18)	136 (11)	4.1 (4)
Na(6)	-1446 (25)	1252 (26)	4844 (17)	3.1 (5)
Na(7)	5810 (18)	3692 (19)	4388 (12)	4.4 (4)
Na(8)	2590 (19)	-3823 (21)	4376 (13)	5.1 (5)
Na(9)	4402 (35)	6904 (37)	913 (24)	5.6 (8)
O <sub>w</sub> (1)	6309 (47)	6263 (51)	148 (32)	8.3 (13)
O <sub>w</sub> (2)	-2755 (24)	-420 (26)	1824 (16)	2.9 (5)
O <sub>w</sub> (3)	-89 (26)	6851 (27)	2688 (18)	3.3 (5)
O <sub>w</sub> (4)	3589 (54)	3796 (58)	2990 (37)	9.9 (16)
O <sub>w</sub> (5)	-3645 (25)	-534 (27)	3801 (17)	3.1 (5)
O <sub>w</sub> (6)	-1260 (24)	-2840 (26)	4284 (16)	2.8 (5)
O <sub>w</sub> (7)	6375 (55)	2367 (60)	265 (38)	10.1 (16)
O <sub>w</sub> (8)	2018 (35)	4701 (37)	4336 (24)	5.5 (8)

Table 1 (cont.)

	x	y	z	B ( $\text{\AA}^2$ )
O <sub>w</sub> (9)	-2509 (23)	6871 (24)	2686 (15)	6.1 (5)
O <sub>w</sub> (10)	1310 (28)	-884 (30)	298 (19)	3.9 (6)
O <sub>w</sub> (11)	4661 (34)	-1161 (37)	123 (23)	5.4 (8)
O <sub>w</sub> (12)	-1919 (25)	-3864 (27)	857 (17)	3.0 (5)
O <sub>w</sub> (13)	5415 (26)	2104 (28)	4437 (18)	3.3 (6)
O <sub>w</sub> (14)	3681 (58)	4902 (63)	1277 (40)	10.7 (17)
O <sub>w</sub> (15)	-1097 (31)	3352 (34)	474 (22)	4.7 (7)
O <sub>w</sub> (16)	6356 (45)	5140 (49)	4488 (31)	8.1 (13)
O <sub>w</sub> (17)	-4450 (27)	-1581 (29)	1443 (18)	3.6 (6)
O <sub>w</sub> (18)	6033 (35)	2340 (38)	2509 (24)	5.5 (8)
O <sub>w</sub> (19)	-480 (28)	7531 (29)	1132 (19)	3.7 (6)
O <sub>w</sub> (20)	4413 (34)	5130 (36)	3553 (23)	5.2 (8)
O <sub>w</sub> (21)	-2742 (43)	3185 (47)	1316 (30)	7.4 (11)
O <sub>w</sub> (22)	5341 (40)	6254 (43)	2079 (27)	6.6 (10)

the scattering factors of O. Nine of these with negative  $B$  values were introduced as  $\text{Na}^+$  ions; their temperature factors became positive. (Only one water molecule has not been found.) In the last cycles a weighting scheme of the form  $w = (330 - 2.35 F_o + 0.0105 F_o^2)^{-1}$  was used. The final  $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.059$  and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.075$ . \* Final atomic coordinates and thermal parameters are listed in Table 1.

All calculations were performed on the Iris 80 computer of the Université Pierre et Marie Curie with a local version of *ORFLS* (Busing, Martin & Levy, 1962) for full-matrix least-squares calculations, *GEST* (de Rango, Tsoucaris, Zelwer & Baudour, 1964) for Fourier syntheses and NRC programs for geometrical calculations (Ahmed, Hall, Pippy & Huber, 1966). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Real and imaginary parts of the anomalous scattering were introduced for W and Si.

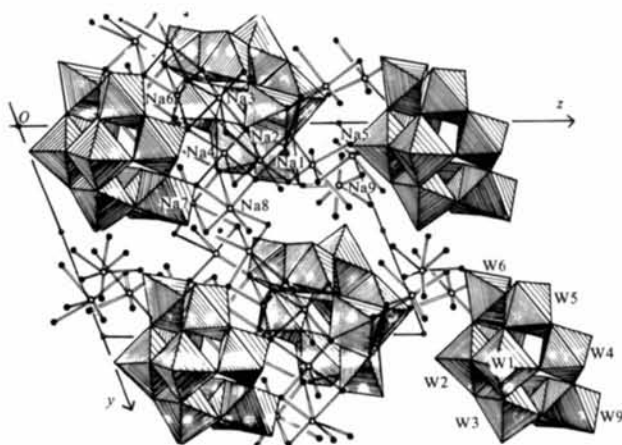
## Discussion

### Description and geometry of the polyanion

In the following discussion, four types of O atoms will be distinguished in the polyanionic structure: O<sub>a</sub> belonging to WO<sub>6</sub> octahedra and to the SiO<sub>4</sub> tetrahedron, O<sub>b</sub> belonging to vertex-sharing octahedra, O<sub>c</sub> belonging to edge-sharing octahedra and O<sub>d</sub> linked to only one W atom. In this last case, if two O<sub>d</sub> are linked to the same W, the prime is added to the O<sub>d</sub> atom *cis* to O<sub>a</sub>.

Each WO<sub>6</sub> octahedron is numbered (Fig. 1) and the number in parentheses following the symbol of an atom

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35726 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 1. Projection of the structure on the  $yz$  plane.

of the polyanion refers to the octahedron to which it belongs. O atoms of water molecules are denoted  $O_w$ .

We have previously distinguished (Tézé & Hervé, 1977) three kinds of  $WO_6$  octahedra, denoted I, II, and III. In the structure of  $\beta$ -enneatungstosilicate only two kinds are observed: those of the three groups of the two edge-sharing  $W_2O_{10}$  [W(4) to W(9)] designated by II; and those of the edge-sharing  $W_3O_{13}$  unit, corresponding to the rotated group of  $\beta$ - $SiW_{12}O_{40}$  [W(1), W(2) and W(3)] designated by III.

The  $\beta$ - $SiW_9O_{34}H^{9-}$  ion is a type A enneapolyanion and appears as a  $\beta$ - $SiW_{12}O_{40}^{4-}$  anion or a  $\beta_1$ - $SiW_{11}O_{39}^{8-}$  one without  $WO_6$  octahedra in site I. An analysis of the geometry shows that, owing to the lack of type I octahedra, some distortions occur (Table 2). These distortions do not appear in the  $W_3O_{13}$  subunit (site III). The mean values of the bond lengths, 2.35 (2) Å for  $W-O_a$ , 1.88 (5) Å for  $W-O_b$ , 1.96 (2) Å for  $W-O_c$  and 1.75 (2) Å for  $W-O_d$ , agree with those found in other Keggin-like structures. On the other hand, in octahedra in site II, the  $W-O_b$  distances involving the  $O_b$ -bridging  $W_3O_{13}$  and  $W_2O_{10}$  subunits are enhanced by about 0.22 Å ( $W-O_b$  mean value 2.12 Å) and the  $W-O_a$  are shortened by 0.1 Å [mean 2.26 (3) Å]. The enhancement of these  $W-O_b$  distances is related to the *trans* effect, due to the fact that there is a double-bonded oxygen  $O'_d$  *trans* to these  $O_b$  instead of a single-bonded one ( $O_c$ ) as in a complete Keggin structure.  $O_a$  is coordinated to Si and only two W atoms, which explains the shortening of the  $W-O_a$  bond.

In the same way, the tetrahedron around Si is slightly flattened on the  $O_a(123)$  vertex and the  $Si-O_a(123)$  bond is a little shorter.

#### Sodium coordination

In the pentamolybdophosphate Strandberg (1973) has observed that  $Mo_5P_2O_{23}$  groups are linked by a

Table 2. Interatomic distances (Å) and angles ( $^\circ$ ) in the  $\beta$ - $SiW_9O_{34}H^{9-}$  anion

The e.s.d.'s are in parentheses.

W(1)— $O_a(123)$	2.32 (3)	W(6)— $O_a(67)$	2.29 (2)
W(1)— $O_b(14)$	1.83 (3)	W(6)— $O_b(26)$	2.13 (3)
W(1)— $O_b(15)$	1.91 (2)	W(6)— $O_b(56)$	1.90 (3)
W(1)— $O_c(12)$	1.94 (2)	W(6)— $O_c(67)$	1.93 (3)
W(1)— $O_c(13)$	1.93 (3)	W(6)— $O_d(6)$	1.72 (2)
W(1)— $O_d(1)$	1.77 (3)	W(6)— $O_d(6)'$	1.77 (3)
W(2)— $O_a(123)$	2.37 (2)	W(7)— $O_a(67)$	2.23 (2)
W(2)— $O_b(26)$	1.86 (2)	W(7)— $O_b(27)$	2.13 (3)
W(2)— $O_b(27)$	1.85 (3)	W(7)— $O_b(78)$	1.88 (3)
W(2)— $O_c(12)$	1.94 (3)	W(7)— $O_c(67)$	1.93 (2)
W(2)— $O_c(23)$	1.98 (3)	W(7)— $O_d(7)'$	1.77 (2)
W(2)— $O_d(2)$	1.75 (2)	W(7)— $O_d(7)$	1.75 (3)
W(3)— $O_a(123)$	2.35 (2)	W(8)— $O_a(89)$	2.26 (2)
W(3)— $O_b(38)$	1.85 (3)	W(8)— $O_b(38)$	2.08 (3)
W(3)— $O_b(39)$	1.96 (2)	W(8)— $O_b(78)$	1.90 (3)
W(3)— $O_c(13)$	1.98 (3)	W(8)— $O_c(89)$	1.92 (2)
W(3)— $O_c(23)$	1.96 (3)	W(8)— $O_d(8)'$	1.78 (2)
W(3)— $O_d(3)$	1.73 (3)	W(8)— $O_d(8)$	1.74 (3)
W(4)— $O_a(45)$	2.23 (2)	W(9)— $O_a(89)$	2.27 (2)
W(4)— $O_b(14)$	2.12 (3)	W(9)— $O_b(39)$	2.21 (2)
W(4)— $O_b(49)$	1.91 (2)	W(9)— $O_b(49)$	1.86 (2)
W(4)— $O_c(45)$	1.92 (3)	W(9)— $O_c(89)$	1.93 (2)
W(4)— $O_d(4)'$	1.75 (2)	W(9)— $O_d(9)'$	1.73 (3)
W(4)— $O_d(4)$	1.76 (3)	W(9)— $O_d(9)$	1.77 (3)
W(5)— $O_a(45)$	2.31 (2)	Si— $O_a(123)$	1.62 (2)
W(5)— $O_b(15)$	2.05 (2)	Si— $O_a(45)$	1.64 (2)
W(5)— $O_b(56)$	1.87 (3)	Si— $O_a(67)$	1.64 (2)
W(5)— $O_c(45)$	1.96 (3)	Si— $O_a(89)$	1.65 (2)
W(5)— $O_d(5)$	1.72 (3)		
W(5)— $O_d(5)'$	1.72 (3)		
		$O_a(123)$ —Si— $O_a(45)$	106.9 (13)
		$O_a(123)$ —Si— $O_a(67)$	109.7 (13)
		$O_a(123)$ —Si— $O_a(89)$	108.4 (13)
		$O_a(45)$ —Si— $O_a(67)$	110.7 (12)
		$O_a(45)$ —Si— $O_a(89)$	110.3 (12)
		$O_a(67)$ —Si— $O_a(89)$	110.7 (12)

network of  $NaO_6$  octahedra formed by water or polyanionic O atoms around a central  $Na^+$  ion. The geometry of the  $\beta$ - $SiW_9O_{34}H^{9-}$  anion, which has a large negative charge and an opened side with a number of double-bonded O atoms, is particularly suited to such a linkage. It occurs by direct O—Na—O bridges between two anions in the *a* and *b* directions, forming through water molecules infinite chains parallel to the *xy* plane. The chains are held together by linkages involving also  $Na^+$  ions and water molecules. For the description of this network (Fig. 1), first let us consider two  $SiW_9O_{34}H^{9-}$  anions related by the inversion centre  $(0,0,\frac{1}{2})$ . They are linked by 10  $Na^+$ . Five are crystallographically independent: Na(4) and Na(6) bind to two  $O'_d$  of each anion; Na(3) and Na(8) bind to two  $O'_d$  of one anion and to one of the other anion; Na(7) binds to one  $O'_d$  of each anion. In addition, Na(3) and Na(7) are linked through a water O atom.

Table 3. *Interatomic distances (Å) around Na<sup>+</sup> ions in the cationic network*

Na(1)—O <sub>d</sub> (2)	2.38 (3)	Na(5)—O <sub>w</sub> (10)	2.38 (5)
Na(1)—O <sub>w</sub> (2)	2.41 (3)	Na(5)—O <sub>w</sub> (15)	2.50 (4)
Na(1)—O <sub>w</sub> (9)	2.41 (3)	Na(5)—O <sub>w</sub> (19)	2.37 (4)
Na(1)—O <sub>w</sub> (12)	2.41 (4)		
Na(1)—O <sub>w</sub> (17)	2.36 (4)	Na(6)—O <sub>d</sub> (8')	2.45 (4)
Na(1)—O <sub>w</sub> (19)	2.37 (5)	Na(6)—O <sub>d</sub> (9')	2.48 (4)
		Na(6)—O <sub>d</sub> (4')	2.51 (4)
Na(2)—O <sub>w</sub> (2)	2.43 (3)	Na(6)—O <sub>d</sub> (5')	2.42 (4)
Na(2)—O <sub>w</sub> (3)	2.44 (4)		
Na(2)—O <sub>w</sub> (5)	2.37 (4)	Na(7)—O <sub>d</sub> (5')	2.35 (3)
Na(2)—O <sub>w</sub> (6)	2.44 (3)	Na(7)—O <sub>d</sub> (8')	2.37 (3)
Na(2)—O <sub>w</sub> (9)	2.41 (4)	Na(7)—O <sub>w</sub> (13)	2.25 (4)
Na(2)—O <sub>d</sub> (7')	2.45 (3)	Na(7)—O <sub>w</sub> (16)	2.32 (7)
		Na(7)—O <sub>w</sub> (20)	2.50 (5)
Na(3)—O <sub>d</sub> (4')	2.38 (3)	Na(7)—O <sub>w</sub> (16)	3.09 (6)
Na(3)—O <sub>d</sub> (7')	2.46 (3)		
Na(3)—O <sub>w</sub> (5)	2.40 (4)	Na(8)—O <sub>d</sub> (9')	2.50 (4)
Na(3)—O <sub>w</sub> (13)	2.38 (4)	Na(8)—O <sub>d</sub> (6')	2.47 (4)
Na(3)—O <sub>w</sub> (18)	2.41 (5)	Na(8)—O <sub>w</sub> (8)	2.33 (5)
Na(3)—O <sub>d</sub> (8)	2.59 (4)	Na(8)—O <sub>w</sub> (20)	2.50 (5)
		Na(8)—O <sub>d</sub> (5')	2.60 (5)
Na(4)—O <sub>d</sub> (4')	2.53 (3)	Na(8)—O <sub>w</sub> (16)	2.48 (6)
Na(4)—O <sub>d</sub> (9')	2.50 (3)		
Na(4)—O <sub>d</sub> (6')	2.41 (3)	Na(9)—O <sub>d</sub> (6)	2.43 (5)
Na(4)—O <sub>d</sub> (7')	2.40 (3)	Na(9)—O <sub>w</sub> (22)	2.48 (7)
Na(4)—O <sub>w</sub> (6)	2.44 (4)	Na(9)—O <sub>w</sub> (1)	2.43 (8)
		Na(9)—O <sub>w</sub> (7)	2.36 (8)
Na(5)—O <sub>d</sub> (7)	2.48 (3)	Na(9)—O <sub>w</sub> (11)	2.48 (6)
Na(5)—O <sub>d</sub> (27)	2.44 (3)	Na(9)—O <sub>w</sub> (14)	2.89 (8)

Now, if we consider two such sets, they are bridged by water O atoms shared by Na(7) or Na(8) and their symmetry-related ions through the inversion point ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ). Therefore, Na<sup>+</sup>[(3),(4),(6),(7),(8)] build an infinite chain stretching in the direction of the *xy* plane.

Lateral chains branched on the previous one are built by Na(1), Na(2) and Na(5). At one end a Na(2) ion is linked to Na(3) and Na(4) (through two O<sub>w</sub>) and to the anion [through O<sub>d</sub>(7)].

At the other end, Na(1) and Na(5) are bonded to one anion of the adjacent main chain by, respectively, one and two O atoms.

Na(9) is bonded to O<sub>d</sub>(6) but is not involved in the network of Na<sup>+</sup> ions. So, the crystal packing is governed in the three directions by all Na<sup>+</sup> ions except Na(9).

Table 3 gives the distances between Na<sup>+</sup> ions and coordinated O atoms. They are in the range 2.32–2.54 Å with three exceptions. Two of these occur in the octahedron around Na(7) (3.09 and 2.25 Å) which is the most distorted one; the third involves Na(9) which has an unexpectedly long distance with O<sub>w</sub>(14) (2.89 Å).

Because of steric hindrance between two polyanions, it is impossible to place two water molecules which would make up an octahedral coordination around Na(4) and Na(6). The theoretical coordinates of such a water molecule, calculated assuming regular octahedra, give too short distances with O<sub>d</sub>(45), O<sub>d</sub>(67) and

O<sub>d</sub>(89) (~2.15 Å). There is no relevant peak on the final difference synthesis at this point.

The Na(5) ion has only five coordinated O atoms. It may be that the sixth belongs to the missing water molecule.

#### Relationship between structure and some chemical behaviour

We previously thought that enneatingstosilicates were of type *B* (Hervé & Tézé, 1977). This assumption was mainly supported by the non-dimerization of enneatingsto polyanions in acidic medium, as opposed to PMo<sub>9</sub>O<sub>34</sub>H<sub>6</sub><sup>3-</sup>, a type *A* polyanion whose structure is known (Pettersson, 1975). This hypothesis was also supported by the visible absorption spectra of reduced derivatives of compounds such as SiW<sub>9</sub>Mo<sub>3</sub>O<sub>40</sub><sup>4-</sup> obtained by addition of molybdate to enneatingstosilicates (Contant, Fruchart, Hervé & Tézé, 1974). In the reduced compounds the Mo → Mo and the Mo → W intervalence transfers occur respectively between intra-groups and extra-groups if the original anion is of type *B* and conversely if it is of type *A*. Fruchart, Hervé, Launay & Massart (1976) interpreted their spectra according to the first viewpoint. The solution of the structure makes it clear that the assignments which correlated the bands of higher energy with the intervalence transfers have to be inverted (Hervé, Tézé & Leyrie, 1979).

This related structure of type *A* closely agrees with the formation of only β<sub>1</sub>-SiW<sub>11</sub>O<sub>39</sub><sup>8-</sup> by addition of two WO<sub>6</sub> octahedra. A structure of type *B* might lead either to β<sub>1</sub> or β<sub>2</sub> isomers, and, as the transformation β<sub>1</sub> → β<sub>2</sub> is irreversible, it is not consistent with obtaining only the β<sub>1</sub> isomer.

The structure of the crystal is probably partially kept in solution by Na<sup>+</sup> ions more or less coupled with the polyanion which decreases its charge. In the crystal structure there is only one water molecule [O<sub>w</sub>(4)] which is not involved in an interaction with a Na<sup>+</sup> ion and this molecule is far from the polyanion. This can be correlated with the fact that polyanions in solutions are not solvated, as shown by ESR (Harmaker & Pope, 1978) and the diffusion rate in solution (Baticle, Perdu & Vennereau, 1967).

#### Conclusion

The structure of the title compound as well as those of the other β isomers agree with the studies of Baker & Figgis (1970) who have previously related the α,β isomerism as a π/3 rotation of a W<sub>3</sub>O<sub>13</sub> group of the Keggin (1934) structure. The structure of α-SiW<sub>9</sub>O<sub>34</sub><sup>10-</sup> can be deduced from the one we solved through a rotation of π/3 of the W<sub>3</sub>O<sub>13</sub> group, and therefore belongs to type *A*.

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