

Multicomponent Polyanions. 24. The Crystal Structure of $\text{Na}_4\text{V}_2\text{O}_7(\text{H}_2\text{O})_{18}$

ARNE BJÖRNBERG

Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

The crystal structure of $\text{Na}_4\text{V}_2\text{O}_7(\text{H}_2\text{O})_{18}$ has been determined from three-dimensional X-ray diffraction data collected with a PAILRED diffractometer using $\text{MoK}\alpha$ -radiation. The crystals are hexagonal, space group $P6_3/m$, with unit cell dimensions $a=9.2478(5)$ and $c=16.591(2)$ Å. The cell contains two formula units. Refinements by full-matrix least-squares methods using anisotropic thermal parameters resulted in a final R -value of 0.061, based on 863 independent reflexions.

The structure is built up from $\text{Na}(\text{H}_2\text{O})_6$ octahedra in two different arrangements: infinite chains of face-sharing octahedra running along the z -axis around $0,0,z$, and $\text{Na}_2(\text{H}_2\text{O})_9$ units centered around $2/3,1/3,1/4$ and $1/3,2/3,3/4$. In the infinite chains, two-thirds of the sodium atomic positions are only half occupied. The chains are held together by hydrogen bonds. In the cavities thus formed (around $2/3,1/3,3/4$ and $1/3,2/3,1/4$) the $\text{V}_2\text{O}_7^{4-}$ anions, which consist of corner-sharing VO_4 tetrahedra, are found. The $\text{V}-\text{O}$ distances vary between 1.530 Å and 1.923 Å, and the $\text{Na}-\text{O}$ distances between 2.307 Å and 2.420 Å. The anion oxygens are all distributed between two positions, the $\text{V}-\text{O}-\text{V}$ angles in each resulting configuration being 124.7° and 117.0° .

Numerous attempts have been made to determine which ions are present in vanadate solutions at different pH values. The region $\text{pH}=10-7$ has been investigated by Ingri, Brito and Sillén,¹ Schwarzenbach and Geier² and more recently by Borgen, Mahmoud and Skauvik,³ all investigators employing different techniques. In the concentration range investigated ($\sim 10^{-2}-10^{-3}$ M) HVO_4^{2-} seems to be the dominating species, but there is evidence for the dimerization of HVO_4^{2-} into $\text{V}_2\text{O}_7^{4-}$ and its protonated form $\text{HV}_2\text{O}_7^{3-}$. Although according to Ref. 2, $\text{V}_2\text{O}_7^{4-}$ is a stronger proton acceptor than

HVO_4^{2-} , no protonated dimer has yet been found in a solid phase. In addition the species HVO_4^{2-} is unknown in the solid state, presumably because of the dominance of the dimer in solutions having a high enough concentration for crystallization.

The $\text{V}_2\text{O}_7^{4-}$ anion has, however, been found in a large number of crystalline substances.⁴ The majority of these are anhydrous compounds grown from oxide melts. Before the present work, the only hydrated divanadate to have its structure solved was $\text{Ca}_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$.⁵ This compound, as well as all the anhydrous ones, contains a $\text{V}_2\text{O}_7^{4-}$ anion consisting of two corner-sharing tetrahedra. Because of the great variation in the surroundings of the anion in the various structures, the configuration of the V_2O_7 unit also shows a wide range of bond distances and angles.

The subject of the present investigation is the crystal structure of $\text{Na}_4\text{V}_2\text{O}_7(\text{H}_2\text{O})_{18}$. It seems probable that the divanadate groups in this crystal have an appearance very close to that in aqueous solution, since the $\text{V}_2\text{O}_7^{4-}$ anions are completely surrounded by water molecules.

This compound was reported for the first time by Roscoe⁶ in 1870.

EXPERIMENTAL

Crystal preparation and analyses. The crystals were prepared by dissolving 7.00 g of $\text{NaVO}_3 \cdot \text{H}_2\text{O}$ in 50 ml of 1.02 M NaOH giving an average charge per vanadium, (z), slightly less than -2.0 . The starting concentration of VO_3^- has to be of the order of 1 M since solutions with the same z value but lower concentrations yield crystals of $\text{NaVO}_3 \cdot 1.89\text{H}_2\text{O}$.⁷ After a few weeks of slow evaporation at room temperature colourless tabular rhombic or

hexagon-shaped crystals were formed. The crystals are extremely unstable in air and will in fact liquefy in a few minutes if left exposed to air at room temperature. During the X-ray exposures they were enclosed, together with part of the mother liquor, in a sealed Lindemann capillary.

The contents of Na and V were determined with the methods given in Ref. 7, the analysis of Na being performed at the Department of Analytic Chemistry, University of Umeå. Found: (weight %) Na 15.9, V 16.0. Calc.: Na 14.6, V 16.2. Water analysis was performed by heating on a thermobalance and gave 50.9 % H₂O (Calc. 51.5 %).

Crystal data. Preliminary Weissenberg and precession photographs showed the diffraction symmetry $6/m$ and systematic extinctions $00l, l = 2n + 1$. The structure was solved using space group $P6_3$, but the resulting structure could equally well be described with space group $P6_3/m$, and this space group was applied in the final refinement.

The unit cell dimensions were refined by least-squares methods from powder photographs taken with a Guinier-Hägg camera using $\text{CuK}\alpha_1$ -radiation ($\lambda = 1.54051 \text{ \AA}$) and with Si as internal standard ($a[\text{Si}] = 5.43054 \text{ \AA}$, $25 \text{ }^\circ\text{C}$). During the exposures the powder was immersed in carbon tetrachloride. The density of the crystals was determined by flotation in a bromoform-carbon tetrachloride solution.

$\text{Na}_4\text{V}_2\text{O}_7(\text{H}_2\text{O})_{18}$
 Space group $P6_3/m$, (No. 176)
 $a = 9.2478(5) \text{ \AA}$, $c = 16.591(2) \text{ \AA}$, $V = 1228.8 \text{ \AA}^3$,
 $\text{F.W.} = 630.12$, $Z = 2$, $D_m = 1.69(1) \text{ g cm}^{-3}$,
 $D_x = 1.703 \text{ g cm}^{-3}$, $\mu(\text{MoK}\alpha) = 9.75 \text{ cm}^{-1}$

Collection and reduction of intensity data. Three-dimensional intensity data were collected at $19 \text{ }^\circ\text{C}$ (the crystals will melt in their own water of crystallization at about $30 \text{ }^\circ\text{C}$, even in a capillary) with a Philips PAILRED linear diffractometer using $\text{MoK}\alpha$ -radiation ($\lambda = 0.71069 \text{ \AA}$), monochromatized with a graphite monochromator. A crystal of approximate dimensions $0.42 \times 0.50 \times 0.21 \text{ mm}$ was mounted and rotated along the y -axis, parallel with the 0.50 mm edge. A total of 4055 reflexions were scanned in the layers $h0l-h12l$ and within $\sin \theta/\lambda \leq 0.80 \text{ \AA}^{-1}$. The measurements were made with scan speed 1° min^{-1} and background time 40 s at the beginning and end of the interval. During the exposure time the intensities decreased by about 29 %, which was compensated for by applying individual layer scale factors which were calculated

* Throughout this paper, numbers in parentheses give the estimated standard deviations and refer to the last decimal place given.

from the intensities of two standard reflexions measured at the beginning and end of each level.

The intensities were corrected for Lorentz and polarization effects and absorption correction was applied ($\mu = 9.75 \text{ cm}^{-1}$) using a $4 \times 12 \times 4$ Gaussian grid. The transmission factor varied between 0.679 and 0.819. For equivalent reflexions a weighted mean value was calculated, and reflexions with a relative statistical error⁸ $\Delta I_0/I_0$ greater than 0.5 were omitted, leaving a total of 968 reflexions.

STRUCTURE DETERMINATION AND REFINEMENT

The vanadium atomic positions were found from a three-dimensional Patterson synthesis, and routine heavy-atom methods revealed the non-hydrogen atoms. Since the two vanadium atoms are situated on a three-fold axis, their oxygen tetrahedra were expected to be oriented with one face perpendicular to the three-fold axis and the bridging oxygen situated on the axis. However, the tetrahedra were found to be tilted with respect to the threefold axis, with the oxygen atoms, for each tetrahedron, in three partly occupied "levels" along the axis. In addition, at each "level" not three but six Fourier peaks were found, indicating that the $\text{V}_2\text{O}_7^{4-}$ group is distributed between two different crystallographic positions (see Fig. 1).

A refinement at this stage with isotropic thermal parameters gave an R -value of 0.100. The refinements were then continued with anisotropic thermal parameters resulting in an R -value of 0.072.

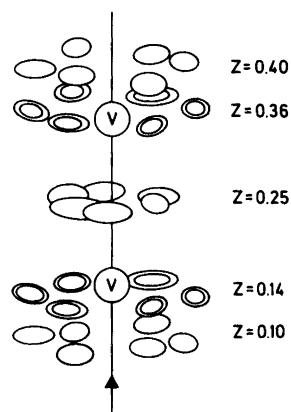


Fig. 1. A schematic drawing of the Fourier map around the V atom. The peaks with double contours have approximately twice the relative height of the single-contoured peaks.

In the difference Fourier synthesis based on the 465 reflexions with $\sin \theta/\lambda \leq 0.52$, the seven highest peaks were all located within acceptable distances from their respective water oxygens and were therefore assigned to hydrogen atoms. Refinement of their positional parameters resulted in unreasonably short O–H distances for two of the water molecules. The only hydrogen to show a relevant coordinate shift was H7 (Table 1) where the H–H distance increased from 0.53 to 1.24 Å giving a much better shape to the Aq4 water molecule. All hydrogen atomic positions, except H7, are therefore given as obtained from the difference Fourier synthesis.

All the vanadate oxygens are in partly occupied positions, and refinements were started with occupancy factors proportional to the relative heights of the respective Fourier peaks. When no restrictions on the total sum of occupancy factors were applied, the result was that the atoms occupying the same *z*-coordinate level, *i.e.* O1/O2 and O3/O4, received the same occupancy factor. For the pair O5/O6 (the bridging oxygen) the results were inconclusive, with one or the other position being more occupied in consecutive refinement runs. All occupancy factors were therefore set at 50/50

probability, employing a model consisting of a rigid V_2O_7 unit being able to rotate around the V–V axis. In a subsequent test run, the deviation from equal probability was 0.5%, which is less than 0.25σ .

In the refinements there were 105 weak reflexions all having a very high F_o/F_c ratio (>2.0), probably due to uncertain background statistics as a consequence of having to use an unusually large crystal. These reflexions were excluded from the refinements.

As previously mentioned, the structure was first solved by applying space group $P6_3$. Owing to the unusually abundant splitting of peaks in the Fourier syntheses, space group $P\bar{6}$ was also tested (neglecting the 00 l -extinction found). Since neither of these approaches resulted in a better fit to the experimental data, there seems to be no reason to assume a lower symmetry than $P6_3/m$.

The refinements finally converged with an *R*-value of 0.061, *R* being defined as $\sum(|F_o| - |F_c|) / \sum|F_o|$ and with $\sum w_i(|F_o| - |F_c|)^2$ as the function minimized. A weighting scheme according to Cruickshank⁹ was applied, $w = (a + |F_o| + c|F_o|^2 + d|F_o|^3)^{-1}$, with $a=200$, $c=0.01$ and $d=0.0025$. In the last cycle of refinement the parameter shifts were less

Table 1. The fractional atomic coordinates. For partially occupied atomic positions the occupancy factors, expressed as fractions of full occupation for the respective positions, are given.

	x	y	z	Occupancy
V	1/3	2/3	0.15121(7)	
O1	0.1931(12)	0.4755(12)	0.1376(9)	1/3
O2	0.1519(19)	0.6248(22)	0.1413(15)	1/3
O3	0.4964(22)	0.7055(22)	0.0824(11)	1/6
O4	0.1589(31)	0.6219(26)	0.0916(10)	1/6
O5	0.2745(27)	0.5596(39)	1/4	1/6
O6	0.2139(57)	0.5738(29)	1/4	1/6
Na1	2/3	1/3	0.3472(1)	
Na2	0	0	0	
Na3	0	0	0.3172(3)	1/2
Aq1	0.4620(4)	0.1240(4)	0.4291(2)	
Aq2	0.4696(4)	0.3301(4)	1/4	
Aq3	0.1996(4)	0.1988(4)	0.0897(2)	
Aq4	0.0160(5)	0.2265(5)	1/4	
H1	0.437	0.025	0.405	
H2	0.478	0.115	0.470	
H3	0.402	0.373	1/4	
H4	0.393	0.244	1/4	
H5	0.290	0.194	0.087	
H6	0.239	0.295	0.065	
H7	0.068(6)	0.305(7)	0.213(3)	

Table 2. The anisotropic thermal parameters ($\times 10^4$). The parameters are calculated according to the formula $\exp[-(h^2\beta_{11} + \dots + 2hk\beta_{12} + \dots)]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
V	136(1)	136(1)	35(0)	68(1)	0	0
O1	137(16)	112(14)	82(7)	20(12)	15(9)	-1(9)
O2	201(25)	368(38)	156(15)	203(26)	28(20)	84(23)
O3	126(26)	164(31)	38(7)	101(24)	-2(11)	12(12)
O4	190(38)	132(28)	27(6)	77(26)	-23(13)	12(11)
O5	223(65)	23(25)	56(15)	-45(42)	0	0
O6	43(28)	228(81)	30(9)	76(40)	0	0
Na1	140(2)	140(2)	22(1)	70(1)	0	0
Na2	134(3)	134(3)	33(1)	67(2)	0	0
Na3	126(4)	126(4)	25(1)	63(2)	0	0
Aq1	218(6)	207(6)	40(1)	114(6)	28(2)	29(2)
Aq2	104(5)	152(6)	36(1)	73(5)	0	0
Aq3	294(6)	202(6)	51(2)	284(5)	-25(2)	-17(2)
Aq4	164(7)	178(8)	53(2)	75(6)	0	0

than 0.2σ for all non-hydrogen atoms.

The atomic scattering factors used for V^{2+} , O^- (vanadate oxygens), O (water oxygens), Na^+ and H were those given by International Tables, Vol. IV.¹⁰ Account was taken of the real and imaginary parts of the anomalous dispersion correction.¹⁰ The computations were performed with a CD CYBER 172 computer at the University of Umeå, with programs given in Ref. 11.

Final atomic positional and thermal parameters are given in Tables 1 and 2. A list of observed and calculated structure factors may be obtained from the author on request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure is built up from $Na(H_2O)_6$ octahedra in two different arrangements: (i) continuous chains of face-sharing octahedra centered around $0,0,z$ and (ii) $Na_2(H_2O)_6$ units centered around $1/3,2/3,3/4$ and $2/3,1/3,1/4$. The $V_2O_7^{4-}$ anions are situated in the cavities thus formed, *i.e.* centered around $1/3,2/3,1/4$ and $2/3,1/3,3/4$. The structure is held together by hydrogen bonds between water molecules and from water molecules to vanadate oxygen atoms.

The divanadate ion. As can be seen from Fig. 2, the divanadate ion consists of two corner-sharing tetrahedra. The anions occupy two crystallographically different positions, one with the oxygen atoms O1—O3—O5 (hereafter called the "odd" position)

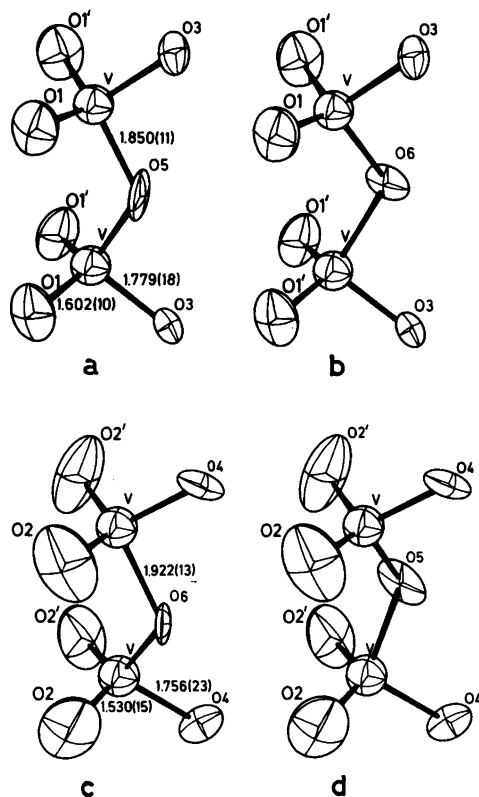


Fig. 2. The four possible configurations of the $V_2O_7^{4-}$ anion. The "twisted" varieties [(b) and (d)] have been included for comparison. The interatomic distances (Å) are given. The thermal ellipsoids are scaled to enclose 50% probability.²⁰

and one with O2–O4–O6 (hereafter called the “even” position). This gives rise to two possibilities of describing the shape and position of the $V_2O_7^{4-}$ anions. The model employed here is that of an ion of fairly definite shape being able to rotate around the V–V axis with a preference for either of six positions with approximately equal surroundings. There is also the possibility of a “flip” in the V–O–V bridge, *i.e.* O5 and O6 could each belong to either of the “odd” and “even” configurations. Assigning O6 to the “odd” or O5 to the “even” configuration will, however, give the $V_2O_7^{4-}$ group a rather twisted shape. Further, the V–O–V angles will deviate more from the tetrahedral angle. Since all other $V_2O_7^{4-}$ structures show comparatively small deviations from this angle the possibility of a “flipping” oxygen bridge is considered unlikely.

Bond angles within the $V_2O_7^{4-}$ ions are given in Tab. 3.

Theoretically there is also the possibility that the two tetrahedra of one $V_2O_7^{4-}$ unit could be situated one in the “even” and the other in the “odd” position. However, since all other $V_2O_7^{4-}$ structures investigated show an approximately eclipsed configuration of the anion, this would seem improbable.

X-Ray films were searched for indications of a superstructure, but since none were found, the conclusion was reached that the two orientations of the $V_2O_7^{4-}$ anions are randomly distributed throughout the crystal. A very similar case was recently described by Catti *et al.*¹² in the structure of β - $Na_2HPO_4 \cdot 12H_2O$, where HPO_4^{2-} anions occupy two different positions around a two-fold axis, surrounded by water hydrogen atoms in an arrangement very similar to this structure.

The V–O distances differ slightly between the “odd” and “even” positions, in the “odd” being between 1.60 Å for two terminal oxygens and 1.85 Å for the bridging oxygen and in the “even” position being between 1.53 and 1.92 Å, respectively. The

Table 3. Bond angles (°) in the divanadate ions.

“Odd” configuration		“Even” configuration	
O1–V–O1'	118.0(3)	O2–V–O2'	118.9(3)
O1–V–O3	108.0(7)	O2–V–O4	109.3(10)
O1–V–O5	105.6(16)	O2–V–O6	92.6(12)
O1'–V–O3	105.6(7)	O2'–V–O4	111.7(10)
O1'–V–O5	115.6(12)	O2'–V–O6	124.2(12)
O3–V–O5	102.8(10)	O4–V–O6	96.9(9)

Table 4. Average V–O distances (Å) found in divanadate structures.

Compound	V–O average	Ref.
α - $Cu_2V_2O_7$	1.709	4
$Ca_2V_2O_7 \cdot 2H_2O$	1.719(V1)	5
	1.716(V2)	
$Co_2V_2O_7$	1.732(V1)	13
	1.734(V2)	
$Ni_2V_2O_7$	1.728(V1)	13
	1.732	
β - $Sr_2V_2O_7$	1.713(V1)	21
	1.725(V2)	
	1.725(V3)	
	1.733(V4)	
$Na_2V_2O_7(H_2O)_{18}$	1.708(“odd”)	
	1.685(“even”)	

distance V–O2 (1.53 Å) is the shortest V–O distance found in a tetrahedral coordination, and is probably slightly erroneous, since the low occupancy factors and large thermal vibrations of the oxygen atoms make the determination of their positions less accurate. The true value is probably closer to 1.57 Å, which would result in an average V–O distance of 1.70 Å for the “even” molecule; a more typical value for $V_2O_7^{4-}$ anions. (Table 4 gives the average V–O distances for a few divanadates.)

Even so, the terminal V–O1 and V–O2 distances found in this structure are unusually short for a four-coordinated vanadium atom. A part of the explanation for this could be the weak interaction from neighbouring atoms, the conditions in this crystal being very much like those in a water solution. (The actual concentration of $V_2O_7^{4-}$ in the crystal is slightly over 3 m.)

The V–O–V angle in divanadate ions shows a large variation due to the influence of surrounding atoms; angles between 117 and 151° have been reported.^{13,14}

There are also a number of structures (often of high-temperature phases) where a 180° angle has been reported.^{15,16} The 180° angle, however, always seems to be a result of a space group of high symmetry (typically $C2/m$). The same pattern can be seen in the diarsenates¹⁷ and diphosphates.^{18,19} The angles in $Na_4V_2O_7(H_2O)_{18}$ are 124.7(13) and 117.0(12)° for the “odd” and “even” positions, respectively. Since the interaction with other atoms in this crystal is comparatively weak and close to uniform in all directions, it seems probable that

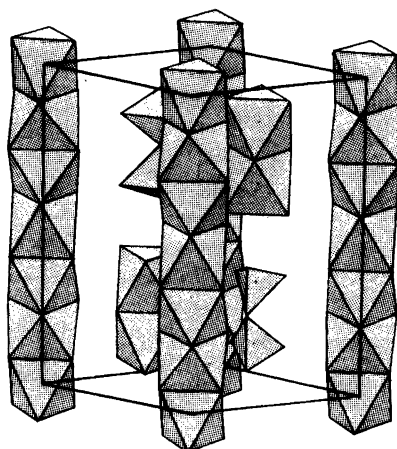


Fig. 3. A view of the coupling of $\text{Na}(\text{H}_2\text{O})_6$ octahedra along the z -axis.

the $\text{V}-\text{O}-\text{V}$ angle in the "free" $\text{V}_2\text{O}_7^{4-}$ anion in solution is close to 120° .

The sodium-water arrangement. All the water molecules are found in octahedral coordination around sodium ions. Infinite chains of face-sharing octahedra run along the z -axis (see Fig. 3). The sodium atoms in these chains are of two different types. Every third octahedron along the axis is occupied by Na2, in 0,0,0 and 0,0,1/2. These octahedra are almost perfectly regular, consisting of six Aq3 atoms at a distance of 2.368(3) Å from the sodium ion. The remaining two-thirds of the octahedron centers along the axis are only half

occupied, Na3 being absent in one or the other in each pair [*i.e.* in (0,0,0.3172) or (0,0,0.1828)] in a random fashion. If Na3 were present in both positions simultaneously, the Na–Na distance would be 2.229(10) Å, which is unreasonably short. As mentioned above, no traces of a superstructure could be found.

The remaining sodium ions and water molecules are found in $\text{Na}_2(\text{H}_2\text{O})_6$ units consisting of two face-sharing octahedra. The Na–O distances in these units are 2.348(4) Å for terminal water molecules and 2.423(3) Å for water molecules coordinated to two sodium atoms.

Bond distances and angles for the non-hydrogen atoms are presented in Table 5.

Hydrogen bonds. The great abundance of water in this structure provides rich opportunities for hydrogen bonds. The water structure is held together mainly by two different bonds, Aq3–H5···Aq1 with an O–O distance of 2.853(5) Å and Aq2–H4···Aq4 with an O–O distance of 2.884(6) Å.

The vanadate ions appear to be well fixed in the "frame" of water molecules. However, as can be seen from Table 6 and Fig. 4, the possibilities of hydrogen bonding from water molecules are as good in either of the "odd" and "even" positions; the table serves well to explain why there appears to be a 50/50 probability of the ion being in either position. There is, in addition, little steric hindrance for the ion to change between these positions.

Acknowledgements. I thank Professor Nils Ingri for much valuable advice and for all the facilities

Table 5. Bond distances (Å) and angles ($^\circ$) in the sodium-water octahedra.

Na1–Aq1	2.348(4)	Aq1–Na1–Aq1	89.85(13)
Na1–Aq2	2.423(3)	Aq1–Na1–Aq2	94.81(10)
Na2–Aq3	2.368(3)	Aq1–Na1–Aq2	94.50(11)
Na3–Aq3	2.404(5)	Aq1–Na1–Aq2	173.62(13)
Na3–Aq4	2.312(4)	Aq2–Na1–Aq2	80.51(10)
Na1–Na1	3.226(5)	Aq3–Na2–Aq3	84.71(12)
Na2–Na3	3.033(5)	Aq3–Na2–Aq3	95.29(12)
		Aq3–Na2–Aq3	180
		Aq3–Na3–Aq3	83.14(18)
		Aq3–Na3–Aq4	90.54(12)
		Aq3–Na3–Aq4	86.57(12)
		Aq3–Na3–Aq4	168.50(21)
		Aq4–Na3–Aq4	98.70(15)

Table 6. Hydrogen bond O—O and O—H distances (Å). Since no hydrogen atomic positions except H7 were refined, no e.s.d.'s for distances involving other hydrogen atoms are available.

"Odd" positions		"Even" positions	
O—O		O—O	
Aq1—H1...O1	2.777(11)	Aq1—H1...O2	2.854(19)
Aq1—H1...O3	2.675(18)	Aq1—H1...O4	2.644(23)
Aq1—H2...O3	2.915(18)	Aq1—H2...O4	2.762(18)
Aq1—H2...O3	3.223(18)		
		Aq2—H3...O2	2.987(19)
		Aq2—H3...O2	2.987(19)
		Aq2—H3...O6	3.087(22)
Aq3—H6...O1	2.709(11)	Aq3—H6...O2	2.768(18)
Aq3—H6...O3	2.779(18)	Aq3—H6...O4	2.710(23)
Aq4—H7...O1	2.774(13)		
Aq4 $\begin{matrix} \text{H7} \\ \diagup \quad \diagdown \\ \text{O5} \end{matrix}$	2.800(30)	Aq4 $\begin{matrix} \text{H7} \\ \diagup \quad \diagdown \\ \text{O6} \end{matrix}$	2.790(31)
		O—H	
Aq2—H4...Aq4	2.884(6)	Aq1—H1	0.92
Aq3—H5...Aq1	2.853(5)	Aq1—H2	0.70
		Aq2—H3	0.89
		Aq2—H4	0.76
		Aq3—H5	0.86
		Aq3—H6	0.87
		Aq4—H7	0.89(5)

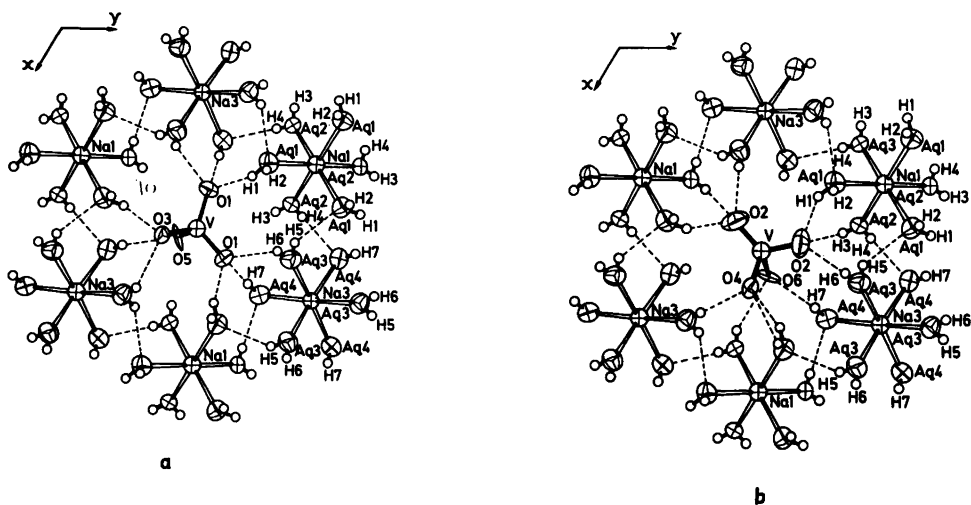


Fig. 4. A projection along the z-axis showing the hydrogen bonds in two of the six possible rotational positions of the anion. Thermal ellipsoids are scaled to enclose 50% probability.²⁰

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