Table 5. *Assumed hydrogen-bond distances* (Å)
$<3 \cdot 15$ Å

The superscripts refer to the following symmetry operations:

(i) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$  (iv) $1-x$, $y$, $\frac{1}{2}-z$

(ii) $\frac{1}{2}-x$, $\frac{1}{2}-y$, $1-z$  (v) $x$, $1-y$, $-\frac{1}{2}+z$

(iii) $\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$  (vi) $\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$.

| | | | |
|---|---|---|---|
| Aq(1)–Aq($3^i$) | 2·935 (12) | Aq(5)–Aq($2^{iii}$) | 2·781 (16) |
| Aq(1)–Aq($4^i$) | 3·110 (14) | Aq(5)–Aq($6b$) | 2·979 (28) |
| | | Aq(5)–Aq($6a$) | 3·067 (23) |
| Aq(2)–O(234) | 2·917 (7) | Aq(5)–Aq(3) | 3·129 (19) |
| Aq(2)–O(3) | 2·985 (8) | | |
| Aq(2)–O($4^{ii}$) | 2·994 (9) | Aq($6a$)–O($356^v$) | 2·895 (19) |
| | | Aq($6a$)–O(2) | 3·000 (20) |
| Aq(3)–O($25^{iii}$) | 2·870 (9) | Aq($6a$)–Aq(3) | 3·097 (21) |
| Aq(3)–O(24) | 2·949 (11) | | |
| | | Aq($6b$)–Aq($6b^{vi}$) | 2·730 (58) |
| Aq(4)–O(6) | 2·777 (13) | Aq($6b$)–O($356^v$) | 2·857 (27) |
| Aq(4)–O(24) | 2·892 (13) | | |
| Aq(4)–Aq($4^{iv}$) | 2·991 (24) | | |

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# Multicomponent Polyanions.
# 26. The Crystal Structure of Na6Mo6V2O26(H2O)16, a Compound Containing Sodium-Coordinated Hexamolybdodivanadate Anions

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### Abstract

$Na_6Mo_6V_2O_{26}(H_2O)_{16}$ is triclinic, $P\bar{1}$, with $a = 10\cdot176$ (2), $b = 10\cdot416$ (4), $c = 10\cdot292$ (2) Å, $\alpha = 113\cdot19$ (2), $\beta = 95\cdot54$ (2), $\gamma = 101\cdot73$ (2)°, $Z = 1$. The structure was refined to a final $R$ of 0·036 based on 5936 independent reflexions. The structure is built up from $Mo_6V_2O_{26}^{6-}$ anions which are linked together by $Na^+$ ions and water molecules in a three-dimensional framework. The anions consist of a flat ring of six edge-sharing $MoO_6$ octahedra with one $VO_4$ tetrahedron on each side capping the hole in the center of the ring. The short Mo—Mo distances are $3\cdot27$–$3\cdot28$ Å and V—Mo distances are $3\cdot71$–$3\cdot77$ Å. The Mo—O distances vary with the number of metal atoms coordinated to each O atom, the average distances being 1·71, 1·91 and 2·35 Å for one-, two- and three-coordinated O atoms respectively. The V—O distances are 1·640 (3) Å for the terminal O atom and 1·78 Å for O atoms shared with Mo.

This study forms part of a project aimed at determining the formation constants and the nature of complexes present in aqueous solutions containing $Mo^{VI}$ and $V^{V}$ (Pettersson, 1979). The interpretation of data from potentiometric titrations is difficult due to the formation of several different polynuclear complexes. Therefore, in order to support the results from the e.m.f. studies, crystallization experiments followed by X-ray structure investigations were started. Several crystalline phases appeared from solutions with different Mo/V ratios, among them $K_8Mo_4V_8^-O_{36}.12H_2O$ which hitherto is the sole example of a structurally determined molybdovanadate (Björnberg, 1979). All solutions having a starting Mo/V ratio $>1$ and $<10$ yield the same compound, $Na_6Mo_6V_2^-O_{26}(H_2O)_{16}$, which is the subject of the present study. The first reports of molybdovanadate salts with a Mo/V ratio of 6:2 date back to that of Liebert (1891). More recent investigations (Bekturov, Ilyasova & Amirbekova, 1970) of the crystallization products from molybdovanadate solutions report the same compound from solutions with a Mo/V concentration ratio $>1$.

The structural type represented by the $Mo_6V_2O_{26}^{6-}$ anion was first proposed by Pettersson (1974) for $Mo_6As_2O_{26}^{6-}$, and has since been found in two anions apart from the present, $(CH_3As)_2Mo_6O_{24}^{4-}$ (Kwak, Rajković, Stalick, Pope & Quicksall, 1976) and the isopolyanion $Mo_8O_{26}^{4-}$ (Fuchs & Hartl, 1976).

## Experimental

### Crystal preparation, analyses and data

In a typical preparation $1.94$ g $NaVO_3.4H_2O$ was dissolved in 30 ml of hot water. $7.26$ g $Na_2MoO_4.2H_2O$ was dissolved in another 30 ml of water. The two solutions were mixed, and $13.33$ ml $3M$ HCl was added dropwise with vigorous stirring. 5 g NaCl was dissolved in this solution which was then filtered at about 313 K. After about 10 d of slow evaporation at room temperature, yellow prismatic crystals formed in the solution. The crystals are unstable in air, and were sealed, with part of the mother liquor, in a Lindemann-glass capillary. Analysis of the crystals gave: Mo $37.5$ and V $7.0$ wt%; calculated: Mo $37.5$ and V $6.7$ wt% (Caven, 1962). Water analysis was performed by

Table 1. *Crystal data for* $Na_6Mo_6V_2O_{26}(H_2O)_{16}$

Triclinic, space group $P\bar{1}$

| | | | |
|---|---|---|---|
| $a$ | = $10.176$ (2) Å | $V$ | = $962.68$ Å$^3$ |
| $b$ | = $10.416$ (4) | $Z$ | = 1 |
| $c$ | = $10.292$ (2) | FW | = $1519.60$ |
| $\alpha$ | = $113.19$ (2)° | $D_x$ | = $2.621$ Mg m$^{-3}$ |
| $\beta$ | = $95.54$ (2) | $D_m$ | = $2.627$ (10) |
| $\gamma$ | = $101.73$ (2) | $\mu$(Mo $K\alpha$) = | $2.473$ mm$^{-1}$ |

heating at 753 K to constant weight in a Pt crucible and gave $18.4$ wt% $H_2O$ (calculated $19.0$ wt%).

From Weissenberg photographs the crystals were found to be triclinic. The density was determined by flotation in a bromoform/carbon tetrachloride solution. Crystal data are given in Table 1.

### Data collection and reduction

A crystal $0.22 \times 0.17 \times 0.35$ mm was chosen. The data were collected at the Department of Inorganic Chemistry, University of Göteborg and Chalmers University of Technology, on a Syntex $P2_1$ automatic four-circle diffractometer with graphite-mono-chromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). The cell parameters were determined by least squares from the setting angles for 15 reflexions.

In the collection of intensities the $\theta/2\theta$ scan method was used, and the $2\theta$ scan speed was allowed to vary between 2 and 8° min$^{-1}$ depending on the intensity of the measured reflexion.

7032 independent reflexions were collected in the region $(\sin \theta)/\lambda < 0.76$ Å$^{-1}$. No separate background measurements were made during data collection. A profile analysis based on the Lehmann & Larsen (1974) method was instead applied to the 96-step profile measured for each reflexion (program $LELA$; Lindqvist & Ljungström, 1979). Correction was made for Lorentz and polarization effects. 5954 reflexions with $F_o^2 \geq 6\sigma(F_o^2)$ were considered as being observed and were used in the subsequent calculations. An absorption correction was applied with a $6 \times 4 \times 8$ Gaussian grid $[\mu(Mo \ K\alpha) = 2.473$ mm$^{-1}]$; the transmission factor varied from $0.654$ to $0.795$.

During data collection the intensities of test reflexions dropped by approximately 29%. This was compensated for by calculating a scale factor from each of the three test reflexions measured between every 40 reflexions. Each intensity was then multiplied by the average scale factor calculated from the three test reflexions. The maximum relative difference between the three scale factors at a given point in the data collection was $\simeq$2%.

### Structure determination and refinement

The Mo and V atoms were located from a Patterson synthesis, and heavy-atom methods gave the positions of the remaining non-hydrogen atoms. Full-matrix least-squares refinement with isotropic temperature factors gave an R of $0.059$, which decreased to $0.045$ when anisotropic temperature factors were applied. As $F_o/F_c$ values showed a tendency to be $>1$ for reflexions with low and high $h$ indices ($h$ being the layer index), and $<1$ for reflexions with intermediate $h$ indices, individual layer scale factors were applied, and refine-

ment finally converged at $R = 0.036$ $(R_w = 0.053)$: $R = \sum ||F_o| - |F_c||/\sum |F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/ \sum w|F_o|^2]^{1/2}$ and $\sum w(|F_o| - |F_c|)^2$ is the function minimized. A weighting scheme according to Cruickshank (1965) was applied; $w = 1/(a + |F_o| + c|F_o|^2 + d|F_o|^3)$ with $a = 125$, $c = 0.01$ and $d = 0.0007$. In the final cycle the parameter shifts were $<0.1\sigma$. As the refinement had to be divided into three blocks, the e.s.d.'s may be somewhat underestimated. The final difference synthesis showed no anomalies. $Mo^{3+}$, $V^{2+}$, $Na^+$, $O^-$ (anion O atoms) and O scattering factors were used

### Table 2. Fractional atomic coordinates $(\times 10^4$; for Mo and V $\times 10^5)$

Numbers in the designation of the anion O atoms denote the metal atom(s) to which each O atom is coordinated.

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| Mo(1) | 13139 (3) | 17077 (3) | 34303 (3) |
| Mo(2) | 12479 (3) | 35458 (3) | 14737 (3) |
| Mo(3) | 1001 (3) | 81866 (3) | 19719 (3) |
| V(4) | 16510 (5) | −1978 (5) | −3807 (5) |
| Na(1) | 3851 (2) | 8418 (2) | 6553 (2) |
| Na(2) | 4615 (2) | 8277 (2) | 39 (2) |
| Na(3) | 1633 (2) | 4804 (2) | 7066 (2) |
| O(1) | 800 (3) | 3034 (3) | 4717 (3) |
| O'(1) | 2738 (3) | 1557 (3) | 4343 (3) |
| O(12) | 2270 (3) | 2821 (3) | 2538 (3) |
| O(13) | −33 (3) | 63 (3) | 3256 (3) |
| O(124) | 365 (3) | 8316 (3) | 8285 (3) |
| O(134) | 1501 (3) | −164 (3) | 1342 (3) |
| O(2) | 2604 (3) | 4537 (4) | 1087 (4) |
| O'(2) | 718 (3) | 4815 (3) | 2822 (3) |
| O(23) | 198 (3) | 6879 (3) | 65 (3) |
| O(234) | 1388 (3) | 1429 (3) | 9599 (3) |
| O(3) | 8760 (3) | 7143 (3) | 2290 (3) |
| O'(3) | 1528 (4) | 8068 (4) | 2883 (4) |
| O(4) | 3175 (3) | −353 (4) | −689 (4) |
| Aq(1) | 4268 (4) | 9518 (4) | 2423 (5) |
| Aq(2) | 2718 (4) | 126 (5) | 6286 (5) |
| Aq(3) | 4977 (3) | 2830 (4) | 2369 (4) |
| Aq(4) | 3825 (5) | 7473 (6) | 3959 (5) |
| Aq(5) | 1849 (4) | 6536 (5) | 6064 (5) |
| Aq(6) | 4080 (4) | 2845 (5) | 8857 (5) |
| Aq(7) | 6068 (4) | 5794 (4) | 3105 (4) |
| Aq(8) | 7356 (4) | 3675 (4) | 467 (4) |
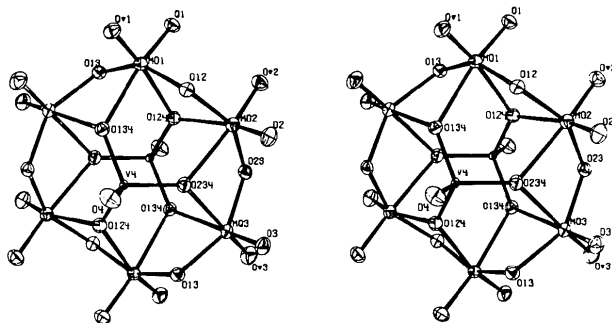


Fig. 1. A stereoscopic view of the $Mo_6V_2O_{26}^{6-}$ anion. The thermal ellipsoids are scaled to enclose 50% probability (ORTEP II; Johnson, 1976).

and account was taken of the real and imaginary parts of the anomalous dispersion (International Tables for X-ray Crystallography, 1974). The programs used have been described by Antti (1976). Computations were performed with the CD Cyber 172 computer at the University of Umeå. Final atomic positional parameters are given in Table 2.*

### Description and discussion of the structure

The crystal is built up from $Mo_6V_2O_{26}^{6-}$ anions, consisting of a ring formed by six edge-sharing $MoO_6$ octahedra. The ring is capped on each side by a $VO_4$ tetrahedron (Fig. 1). The anions are joined in a three-dimensional framework by $Na^+$ ions and hydrogen bonds from water molecules. $Na^+$ ions take part in both O—Na—O and O—Na—Aq—Na—O bonds. The anions are spaced relatively far apart; the shortest O—O distance between O atoms in different anions is $3.152$ (4) Å [O(1)—O(3)], which can be compared to the shortest O—O distance between adjacent anions in $K_8Mo_4V_8O_{36} \cdot 12H_2O$ (Björnberg, 1979) which is $2.814$ Å. This clearly shows the better ability of $Na^+$ to coordinate O atoms. With $K^+$ as the cation, anions tend to form a close-packed structure, where the cations occupy positions having minimum steric hindrance. The distance $2.814$ Å is very close to the sum of the van der Waals radii (Pauling, 1960).

### The $MoO_6$ octahedra and $VO_4$ tetrahedra

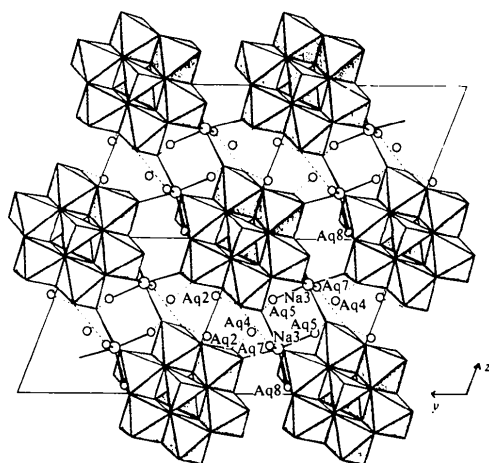Table 3 shows that the $MoO_6$ octahedra are somewhat distorted, and the Mo—O distances show the normal variation according to the number of metal atoms coordinated to each O atom (Hedman, 1978). All three independent octahedra have very similar Mo—O distances and angles. The variations for the three different groups of bonds are only $1.706–1.726$ Å for terminal O atoms, $1.898–1.925$ Å for O atoms shared between two metal atoms and $2.313–2.383$ Å for O atoms coordinated to three metal atoms, with average bond lengths of $1.714$, $1.910$ and $2.335$ Å for the three groups respectively. [The bond lengths are well outside the average $(\pm 3\sigma)$ only for the three-coordinated O atoms.] The $VO_4$ tetrahedra are very close to being regular, with all three bonds to three-coordinated O atoms within $1\sigma$ of their average length and bond angles within $1°$ of the tetrahedral angle.

This anion is isostructural with $Mo_8O_{26}^{4-}$ described by Fuchs & Hartl (1976). As in the octamolybdate anion,

Table 3. *Distances (Å) and angles (°) within the* $Mo_6V_2O_{26}^{6-}$ *anion*

|            | O(1)      | O'(1)     | O(12)     | O(13)     | O(124)    | O(134)    |
|------------|-----------|-----------|-----------|-----------|-----------|-----------|
| Mo(1)–     | 1·710 (3) | 1·718 (3) | 1·920 (3) | 1·898 (3) | 2·324 (3) | 2·320 (3) |
| O(1)–      |           | 2·705 (4) | 2·777 (4) | 2·753 (4) | 2·850 (4) |           |
| O(134)–    |           | 2·883 (4) | 2·757 (4) | 2·598 (4) | 2·893 (4) |           |
| O'(1)–     |           |           | 2·724 (4) | 2·804 (4) |           |           |
| O(124)–    |           |           | 2·606 (4) | 2·778 (4) |           |           |
| O(1)–Mo(1)–   |        | 104·2 (2) | 99·6 (1)  | 99·3 (1)  | 88·6 (1)  | 165·8 (1) |
| O(134)–Mo(1)– |        | 89·8 (1)  | 80·5 (1)  | 75·3 (1)  | 77·8 (1)  |           |
| O'(1)–Mo(1)–  |        |           | 96·8 (1)  | 101·6 (1) | 166·0 (1) |           |
| O(124)–Mo(1)– |        |           | 75·1      | 81·6 (1)  |           |           |

|            | O(2)      | O'(2)     | O(12)     | O(23)     | O(124)    | O(234)    |
|------------|-----------|-----------|-----------|-----------|-----------|-----------|
| Mo(2)–     | 1·726 (3) | 1·719 (3) | 1·898 (3) | 1·898 (3) | 2·383 (3) | 2·331     |
| O(2)–      |           | 2·727 (4) | 2·738 (4) | 2·823 (4) |           | 2·909 (4) |
| O(124)–    |           | 2·919 (4) | 2·606 (4) | 2·782 (4) |           | 2·912 (4) |
| O'(2)–     |           |           | 2·801 (4) | 2·735 (4) |           |           |
| O(234)–    |           |           | 2·748 (4) | 2·572 (4) |           |           |
| O(2)–Mo(2)–   |        | 104·7 (2) | 98·0 (1)  | 102·2 (1) | 165·3 (1) | 90·3 (1)  |
| O(124)–Mo(2)– |        | 89·2 (1)  | 74·0 (1)  | 80·2 (1)  |           | 76·3 (1)  |
| O'(2)–Mo(2)–  |        |           | 101·4 (1) | 98·1 (1)  |           | 164·4 (1) |
| O(234)–Mo(2)– |        |           | 80·3 (1)  | 74·1 (1)  |           |           |

|            | O(3)      | O'(3)     | O(13)     | O(23)     | O(134)    | O(234)    |
|------------|-----------|-----------|-----------|-----------|-----------|-----------|
| Mo(3)–     | 1·707 (3) | 1·706 (4) | 1·921 (3) | 1·925 (3) | 2·337 (3) | 2·313 (3) |
| O(3)–      |           | 2·709 (5) | 2·759 (4) | 2·788 (4) |           | 2·886 (4) |
| O(134)–    |           | 2·868 (5) | 2·598 (4) | 2·791 (4) |           | 2·861 (4) |
| O'(3)–     |           |           | 2·797 (5) | 2·741 (5) |           |           |
| O(234)–    |           |           | 2·775 (4) | 2·572 (4) |           |           |
| O(3)–Mo(3)–   |        | 105·1 (2) | 98·8 (1)  | 100·2 (1) | 165·5 (1) | 90·5 (1)  |
| O(134)–Mo(3)– |        | 89·0 (1)  | 74·5 (1)  | 81·2 (1)  |           | 75·9 (1)  |
| O'(3)–Mo(3)–  |        |           | 100·7 (2) | 97·9 (2)  |           | 163·7 (1) |
| O(234)–Mo(3)– |        |           | 81·3 (1)  | 74·1 (1)  |           |           |

|            | O(4)      | O(124)    | O(134)    | O(234)    |         | Mo(1)     | Mo(2)     | Mo(3)     | V(4)      |
|------------|-----------|-----------|-----------|-----------|---------|-----------|-----------|-----------|-----------|
| V(4)–      | 1·640 (3) | 1·775 (3) | 1·782 (3) | 1·776 (3) | Mo(1)–  | 6·509 (2) | 3·284 (1) | 3·270 (1) | 3·712 (1) |
| O(4)–      |           | 2·805 (4) | 2·795 (4) | 2·808 (4) | Mo(2)–  | 5·668 (2) | 6·592 (2) | 3·275 (1) | 3·736 (1) |
| O(124)–    |           |           | 2·893 (4) | 2·912 (4) | Mo(3)–  | 5·657 (1) | 5·701 (2) | 6·559 (1) | 3·729 (1) |
| O(134)–    |           |           |           | 2·861 (4) | V(4)–   | 3·721 (1) | 3·770 (1) | 3·749 (1) | 3·591 (1) |
| O(4)–V(4)–     |       | 110·4 (2) | 109·5 (2) | 110·5 (2) |         |           |           |           |           |
| O(124)–V(4)–   |       |           | 108·9 (1) | 108·7 (1) |         |           |           |           |           |
| O(134)–V(4)–   |       |           |           | 108·8 (1) |         |           |           |           |           |



Fig. 2. The coordination around Na(3) projected along $x$. Dashed lines are probable hydrogen bonds.

$Mo_6V_2O_{26}^{6-}$ can be described as being built up from a $Mo_6O_{18}$ neutral ring of corner-sharing tetrahedra, with two more tetrahedra attached to each side of the ring. The most perceptible difference in bond lengths is that the distances from the ring Mo atoms to the three-coordinated O atoms are shorter in $Mo_6V_2O_{26}^{6-}$ than in the octamolybdate, where this average distance is 2·454 Å. This could be explained by the smaller electrostatic repulsion between $V^V$ and $Mo^{VI}$ than between two $Mo^{VI}$, since the $M$–O distances are very similar in the $VO_4$ tetrahedra and in the capping $MoO_4$ tetrahedra in $Mo_8O_{26}^{4-}$.

### The coordination around sodium ions

The structure contains three crystallographically different $Na^+$ ions, which all coordinate six anion or water O atoms. The octahedra are not exceptionally irregular, except for the coordination around Na(1)
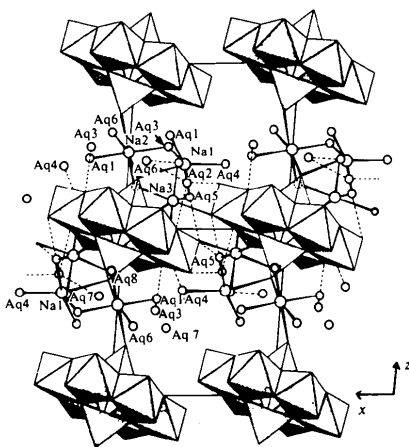
Fig. 3. The coordination around the Na$^+$ ions projected along $y$. For clarity only one of each Na$^+$ ion has been drawn in the same unit cell.

Table 4. *Sodium–oxygen distances* (Å)

| Na(1)–Aq(1) | 2·356 (4) | Na(3)–O(1) | 2·328 (3) |
|---|---|---|---|
| Aq(5) | 2·376 (5) | O(3) | 2·343 (4) |
| Aq(2) | 2·392 (5) | Aq(8) | 2·383 (4) |
| Aq(3) | 2·420 (4) | Aq(5) | 2·391 (5) |
| Aq(4) | 2·450 (5) | O'(2) | 2·509 (4) |
| O(4) | 2·836 (4) | Aq(7) | 2·545 (5) |
| Na(2)–Aq(1) | 2·381 (5) | | |
| Aq(8) | 2·395 (4) | | |
| Aq(3) | 2·406 (5) | | |
| Aq(6) | 2·410 (5) | | |
| O(4) | 2·495 (4) | | |
| O(4) | 2·603 (4) | | |

Table 5. *Probable hydrogen-bond* (O–O) *distances* (Å)

| Aq(1)–O(134) | 3·057 (5) | Aq(5)–O(1) | 2·911 (5) |
|---|---|---|---|
| O'(3) | 3·064 (5) | O'(2) | 3·063 (6) |
| O'(1) | 3·078 (5) | O(124) | 3·068 (5) |
| Aq(2)–O(13) | 2·798 (5) | Aq(6)–Aq(2) | 2·956 (7) |
| O'(1) | 2·927 (5) | O(3) | 3·019 (5) |
| | | O(2) | 3·031 (6) |
| Aq(3)–O(12) | 2·775 (4) | Aq(7)–O'(1) | 2·881 (5) |
| Aq(7) | 2·818 (6) | Aq(6) | 2·897 (7) |
| | | Aq(4) | 3·137 (7) |
| Aq(4)–O'(3) | 2·775 (6) | | |
| Aq(1) | 3·105 (7) | Aq(8)–O(23) | 2·725 (4) |
| | | O(2) | 2·890 (5) |

which has a rather long Na(1)–O(4) distance of 2·836 (4) Å. Both Na(2) and Na(3) connect two anions. The anion O atoms coordinated to the Na$^+$ ions are all terminal. No systematic difference between Na–O(water) distances and Na–O(anion) atom distances can be seen.

Four of the water O atoms are coordinated to two Na$^+$ ions, thus strengthening the coupling between anions by the creation of O–Na–Aq–Na–O bridges (Figs. 2 and 3).

The Na–O distances are given in Table 4.

## The water molecules

All water molecules are coordinated to Na$^+$ ions. In addition, the Aq–O and Aq–Aq distances indicate that all water molecules take part in hydrogen bonds forming a network through the structure. Attempts were made to locate the H atoms, which were found at 14 of the expected 16 sites from peaks in a difference synthesis. Their height and the low degree of success of refinement of H atom positions, however, did not justify inclusion of the H atom coordinates in the description of the structure. Probable hydrogen-bond distances are given in Table 5.

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