The Crystal Structure of $NaVO_3.1.89H_2O$

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The crystal structure of $NaVO_3.1.89H_2O$ has been determined from three-dimensional X-ray diffraction data collected with a PAILRED diffractometer using $MoK\alpha$-radiation. The crystals are monoclinic, space group $P2_1/a$ (No. 14), with unit cell dimensions $a = 16.756(2)$ Å, $b = 3.6391(3)$ Å, $c = 8.023(1)$ Å, $\beta = 111.18(1)°$ and the cell contains four formula units. Refinement by full-matrix least-squares methods using anisotropic thermal parameters resulted in a final R-value of 0.023, based on 1307 independent reflexions.

In the structure each vanadium atom is surrounded by five oxygen atoms forming a distorted trigonal bipyramid. Each bipyramid shares two edges forming continuous chains parallel with the y-axis. The chains are held together in the z direction by $O-Na\genfrac{}{}{0pt}{}{O}{O}$ bridges and in the x direction by hydrogen bonds involving the water molecules. One of the two water positions is only partly occupied with an occupancy factor of 0.89(1). The $V-O$ distances are 1.643(1) and 1.653(1) Å for unshared oxygen atoms and 1.882(3), 1.928(3) and 1.988(1) Å for shared oxygens, while the $Na-O$ and $Na-Aq$ distances vary between 2.37 and 2.46 Å.

Numerous attempts have been made to determine which ions are present in vanadate solutions at different pH-values. Aqueous equilibrium studies using potentiometric methods have indicated that the pH-range $0-14$ can be divided into different regions depending on the composition of the species. A critical review of the equilibrium studies and the species found has recently been given by Baes and Mesmer.[1] One of the regions, the metavanadate region ($6 \lesssim pH \lesssim 9$), is very complicated to investigate with these methods, due to slow equilibria and low solubility. The general formula of the metavanadates $(VO_3^-)_n$ has been established, however, and two anions,

$V_3O_9^{3-}$ and $V_4O_{12}^{4-}$, have been suggested.[2-4] Work is at present in progress at this department to further establish equilibria and dominating species in this region.[5]

Parallel with these investigations, crystallization experiments followed by X-ray structure investigations have been performed in order to support the results of the equilibrium studies. However, with Na^+, K^+, Ca^{2+}, Sr^{2+} or NH_4^+ as cations only structures with infinite metavanadate chains are found. Crystals containing the $V_3O_9^{3-}$ or $V_4O_{12}^{4-}$ anions have so far not been obtained from aqueous solutions, but by dissolution of V_2O_5 in an ethanolic tetrabutylammonium hydroxide solution followed by recrystallization in acetone on addition of benzene, the compound $[N(C_4H_9)_4]_3HV_4O_{12}$ has recently been isolated.[6] The structure determination was not completed, but the structure of the V_4O_{12} group is similar to that of the tetrametaphosphate ion, $P_4O_{12}^{4-}$.[7]

The subject of the present investigation is the crystal structure of a sodium metavanadate, $NaVO_3.1.89H_2O$, which is of interest for the systematic studies of vanadates in our department. Apart from information on the metavanadate chains the crystal structure can explain the non-stoichiometry for the water of crystallization. This compound has been referred to as $NaVO_3.1.9H_2O$ by Lukács and Strusievici[8] (powder diffraction, IR, DTA), but usually it has been assigned the composition $NaVO_3.2H_2O$.[9]

EXPERIMENTAL

Crystal preparation and analyses. In a typical preparation 0.455 g of V_2O_5 was dissolved in 100 ml of 0.060 M NaOH giving an average charge per vanadium, (z), equal to -1.2. Then

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0.001 mol of perchloric acid was added, raising the z value to -1.0 (the same as in the metavanadate anions, $(VO_3^-)_n$). After a few days (sometimes weeks) of slow evaporation at room temperature, white or colourless acicular crystals were formed, often grown together forming a thistle-like arrangement. The crystals are unstable in air and during the X-ray exposures they were enclosed, together with part of the mother liquor, in a sealed Lindemann capillary.

The contents of Na (by atomic emission) and V (by reduction with $Fe(NH_4)_2(SO_4)_2$, addition of H_3PO_4 and titration with MnO_4^-) were determined, the analyses being performed at the Analytical Laboratory, Boliden AB, Skelleftehamn. Found: (weight %) Na 14.3; V 32.6. Calc. for $NaVO_3 . 1.89H_2O$: Na 14.7; V 32.7. Water analysis was performed with the Penfield method [10] and gave 21.4 % H_2O (calc. 21.8 %). The water analysis gives the formula $NaVO_3 . 1.86H_2O$, which is in fair agreement with the occupancy factor refined from X-ray data.

Crystal data. Preliminary Weissenberg and precession photographs showed the crystal system to be monoclinic. Systematic extinctions $h0l$, $h = 2n + 1$ and $0k0$, $k = 2n + 1$ uniquely determined the space group as $P2_1/a$. However, all hkl $(k \neq 0)$ reflexions with $h = 2n + 1$ were very weak, indicating the structure to be very close to space group $P2_1/m$ with a sub-cell where $a = 8.378$ Å. As can be seen from Table 1, the y-coordinates of all non-hydrogen atoms are close to $1/4$.

The unit cell dimensions were refined by least-squares methods [11] from powder photographs taken with a Guinier-Hägg camera using $CuK\alpha_1$-radiation $(\lambda = 1.54051$ Å) and with $Pb(NO_3)_2$ as internal standard $(a[Pb(NO_3)_2] = 7.8575$ Å, $25 °C)$. The density of the crystals was determined by flotation in a bromoform/carbon tetrachloride solution.
$NaVO_3 . 1.89H_2O$
Space group $P2_1/a$, (No. 14), all atoms in $4(e)$:
$\pm (x,y,z; \; 1/2+x, 1/2-y, z)$
$a = 16.756(2)$ Å, $b = 3.6391(3)$ Å, $c = 8.023(1)$ Å,
$\beta = 111.18(1)°$, $V = 456.2$ Å^3, F.W. $= 155.98$,
$Z = 4$, $D_m = 2.28(1)$ g cm^{-3}, $D_x = 2.27$ g cm^{-3},
$\mu(MoK\alpha) = 23.15$ cm^{-1}

Collection and reduction of intensity data. The structure was solved from a preliminary data set, collected with equi-inclination Weissenberg film methods, using $CuK\alpha$-radiation $(\lambda = 1.5418$ Å). The intensities of 398 independent reflexions from the layers $h0l - h2l$ were estimated visually. In order to obtain more accurate intensity values for the weak $h = 2n + 1$ reflexions and determine the full structure, three-dimensional intensity data were collected at $25 °C$ with a Philips PAILRED linear diffractometer using $MoK\alpha$-radiation $(\lambda = 0.71069$ Å) monochromatized with a graphite monochromator. A crystal of approximate dimensions $0.10 \times 0.18 \times 0.15$ mm was mounted and rotated along the y-axis, which was parallel with the 0.18 mm edge. A total of 1584 unique reflexions were scanned in the layers $h0l - h6l$ and within $(\sin \theta)/\lambda = 0.86$ Å^{-1}. The measurements were made with scan speed 1° min^{-1} and background time 40 s at the beginning and end of the interval.

Reflexions with a relative statistical error [12] $\Delta I_0/I_0$ greater than 0.5 were omitted leaving a total of 1325 reflexions. The intensities were corrected for Lorentz and polarization effects, and absorption correction was applied $(\mu = 23.15$ cm$^{-1})$ using a $4 \times 8 \times 6$ Gaussian grid. The transmission factor varied between 0.721 and 0.822.

STRUCTURE DETERMINATION AND REFINEMENT

Since all reflexions with $h = 2n + 1$ were very weak, the structure, when first determined from film data, was based on the sub-cell with $a = 8.378$ Å and space group $P2_1/m$. The vanadium atomic position was found from a three-dimensional Patterson synthesis, and routine heavy-atom methods revealed the non-hydrogen atoms, all atoms being in position $2(e)$. This structure was refined with isotropic thermal parameter to an R-value of 0.156.

With diffractometer data, including the weak $h = 2n + 1$ reflexions, the a parameter was doubled to 16.756 Å changing the space group to $P2_1/a$. The refinements were started with the film-data parameters, and with isotropic temperature factors they converged at $R = 0.101$. The refinements were then continued with anisotropic thermal parameters resulting in an R-value of 0.036.

A difference Fourier synthesis showed a weak negative peak at the same position as one of the water oxygens. The occupancy factor for this atom was therefore refined resulting in a value of 0.89(1), which is in fair agreement with the result of the water analysis.

From a difference Fourier synthesis based on the 372 reflexions with $(\sin \theta)/\lambda < 0.5$ Å^{-1} two peaks around Aq1 were found, while near the partly occupied Aq2 position, only one well-defined peak appeared. These three peaks were taken as hydrogen atoms and included in the refinements. The β_{22} parameter for Aq2 is abnormally large and may well include the effects from an unresolved second hydrogen atom. Attempts to split the Aq2 position into

two partly occupied oxygen atomic positions, as well as into one oxygen and one hydrogen atomic position caused the refinements to diverge.

Since for the strongest reflexions F_c was greater than F_o, an isotropic secondary extinction parameter was included as described by Coppens and Hamilton,[13] this parameter receiving a value of $g' = 0.77(4)$. The refinements finally converged with an R-value of 0.023, 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 Cruickshank[14] was applied, $w = (a + |F_o| + c|F_o|^2 + d|F_o|^3)^{-1}$, with $a = 600$, $c = 0.2133$ and $d = 0.008$. In the last cycle of refinement the parameter shifts were less than 0.25σ for all non-hydrogen atoms.

The atomic scattering factors used for V^{3+}, O, O^-, Na^+ and H were those given by International Tables, Vol IV.[15] Account was taken of the real and imaginary parts of the anomalous dispersion correction. The computations were performed with a CDC 3300 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 can be obtained from the authors on request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure is built up from continuous chains, parallel with the y-axis, consisting of vanadium-oxygen trigonal bipyramids sharing edges. These chains are held together in the z-direction by $O - Na\begin{smallmatrix} O \\ \diagdown \\ O \end{smallmatrix}$ bridges. The coordination around the sodium atoms is octahedral, with three vanadate oxygens and three water oxygens coordinated to each sodium atom. The layers thus formed are held

Table 1. The fractional atomic coordinates and, for the hydrogen atoms, the isotropic temperature factors ($Å^2$). The estimated standard deviations are given in parentheses.

	x	y	z	B
V	0.03783(2)	0.2455(2)	0.16781(3)	
O1	0.00071(8)	0.2510(10)	0.3327(1)	
O2	0.14265(9)	0.2780(10)	0.2540(2)	
O3	0.98668(9)	0.2479(8)	0.9023(1)	
Na	0.09375(5)	0.2520(7)	0.6478(1)	
Aq1	0.32282(8)	0.2581(14)	0.4108(2)	
Aq2	0.18965(16)	0.2423(23)	0.9491(3)	
H1	0.272(2)	0.198(13)	0.369(4)	2.8(7)
H2	0.333(2)	0.201(15)	0.511(5)	3.8(8)
H3	0.167(4)	0.361(23)	0.018(9)	7.8(19)

Table 2. The final anisotropic thermal parameters ($\times 10^4$) with their estimated standard deviations ($\times 10^4$) in parentheses. The parameters are calculated according to the formula $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
V	14(0)	149(1)	35(0)	11(1)	7(0)	3(2)
O1	22(0)	295(7)	60(1)	−8(7)	20(1)	12(13)
O2	15(0)	474(17)	97(2)	−12(3)	11(1)	−25(7)
O3	40(1)	156(6)	43(1)	3(6)	7(1)	59(9)
Na	22(0)	378(6)	119(1)	24(4)	9(0)	−8(9)
Aq1	18(0)	650(13)	90(2)	−10(7)	12(1)	15(16)
Aq2	31(1)	3841(110)	120(4)	117(20)	29(2)	187(39)

together in the x-direction by hydrogen bonds, which accounts for the extremely good (100) cleavage.

The vanadium-oxygen arrangement. As can be seen from Fig. 1, each vanadium atom is surrounded by five oxygen atoms in a distorted trigonal bipyramidal arrangement. The inter-atomic $V-O$ distances are longer (1.88 – 1.99 Å) to the three oxygen atoms which are shared between two or three vanadium atoms, than to the two unshared oxygens (1.64 – 1.65 Å). The apexes of the trigonal bipyramid are out of line with the vanadium atom; the $O3-V-O3$ angle is 145.54(7)°. As can be seen from Table 1, the vanadium atom is not in the same plane as the three equatorial oxygen atoms. All atoms slightly offset from $y = 1/4$, thus giving rise to the weak $h = 2n + 1$ reflexions. In KVO_3. H_2O [16] all atoms are in $z = 1/4$ as a result of the space group symmetry ($Pnam$) and the vanadium atom in that compound lies in the plane of the oxygen atoms. The trigonal bipyramids share edges to form chains parallel with the y-axis. The $V-V$ distances within the chain are 3.096(1) and 3.134(1) Å.

The results show that the vanadate chains in this structure look very much like those reported in $KVO_3.H_2O$,[16] $Ca(VO_3)_2.4H_2O$ [17] and $Sr(VO_3)_2.4H_2O$.[18]

There seem to be two distinctly different kinds of five-coordinated vanadium, one being trigonal bipyramidal as in $NaVO_3 . 1.89H_2O$ or $KVO_3.H_2O$, and one square pyramidal, e.g. in CsV_3O_8.[19] The two configurations can most easily be distinguished by the $V-O$ distances. In the trigonal bipyramid, there are two short (< 1.68 Å) and three long (> 1.85 Å) bonds,
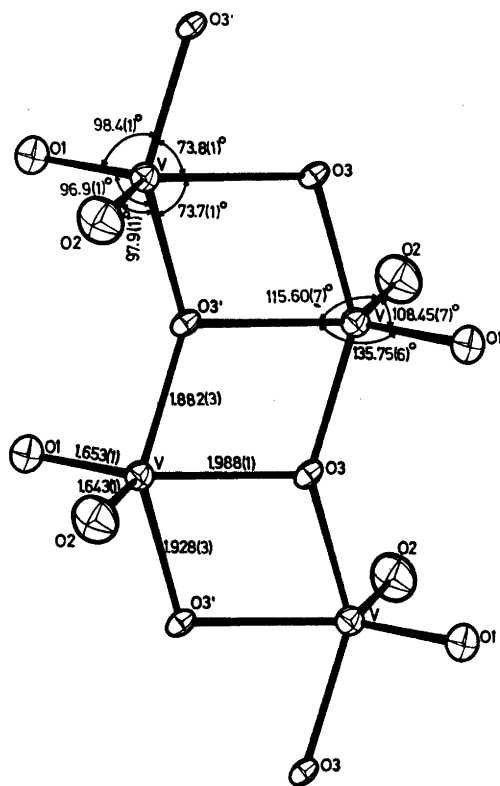

Fig. 1. The vanadium-oxygen coordination. The interatomic distances (Å) and angles (°) are given, with the e.s.d.'s in parentheses referring to the last decimal place given. The angle $O3'-V-O2$ from the top $O3'$ atom is 106.2(1)°. The thermal ellipsoids are scaled to enclose 50 % probability.[21]
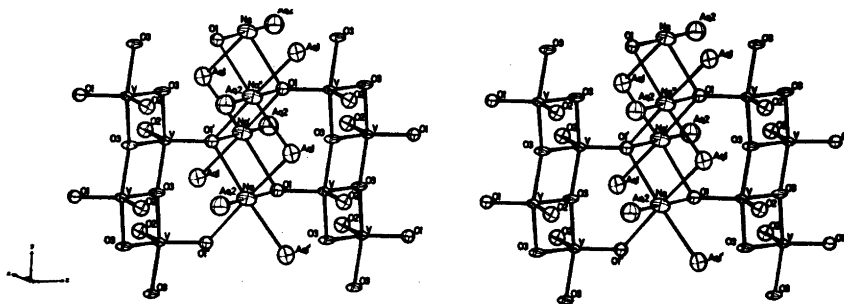

Fig. 2. A stereoscopic view of the layer structure created by vanadium-oxygen-sodium. The thermal ellipsoids are scaled to enclose 50 % probability,[21] except for Aq2, which is drawn as a sphere of radius 0.22 Å. The magnitude of the real β_{22} would cause Aq2 to obscure large parts of the drawing.

Table 3. Distances (Å) and angles (°) within the $NaO_3(H_2O)_3$ octahedra. The designation of the atoms refers to the bottom octahedron in Fig. 2. The estimated standard deviations are given in parentheses and refer to the last decimal place given.

Na − Aq1	2.458(4)		Na − O1′	2.445(3)
Na − Aq1′	2.425(4)		Na − O1″	2.462(3)
Na − O1	2.444(1)		Na − Aq2	2.371(3)
Na − Na″	3.6391(3)			
Na − Na′	3.671(3)			
Na′ − Na″	3.656(3)			
O1′ − Na − O1″	95.74(5)		O1 − Na − O1′	83.19(9)
O1″ − Na − Aq1′	83.69(13)		O1 − Na − O1″	83.11(9)
Aq1′ − Na − Aq1	96.36(6)		O1 − Na − Aq1′	89.74(9)
Aq1 − Na − O1′	83.34(13)		O1 − Na − Aq1	89.87(9)
Aq2 − Na − O1′	99.30(17)			
Aq2 − Na − O1″	97.96(17)		Aq2 − Na − O1	177.16(11)
Aq2 − Na − Aq1′	87.76(16)			
Aq2 − Na − Aq1	89.05(17)			

while in the square pyramid there are one short apical bond and four long (1.75 − 2.00 Å) bonds. Distances and angles within the vanadate chain are given in Fig. 1.

The sodium-oxygen arrangement. The Na⁺-ion coordinates six oxygen atoms in an octahedral arrangement, which can be written $NaO_3(H_2O)_3$. These octahedra are linked together by sharing edges to form continuous double chains in between and parallel with the vanadate chains. The oxygen atoms shared with vanadium are always O1, the bridge between two vanadium

atoms being V − O1 ⟨Na Na⟩ O1 − V. The water

molecules in an octahedron are two Aq1, both bonded to two Na⁺-ions, and one Aq2 which is bonded to only one Na⁺. A detail of the resulting layer structure is shown in Fig. 2. The octahedra are not very far from regular, with Na − O distances varying between 2.37 and 2.46 Å. Distances and angles within the sodium-oxygen octahedra are given in Table 3.

Hydrogen bonding. The layers mentioned above are held together by hydrogen bonds from water molecules to O2, which for spatial reasons is the only oxygen atom available
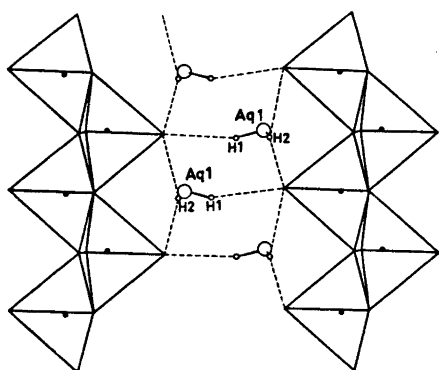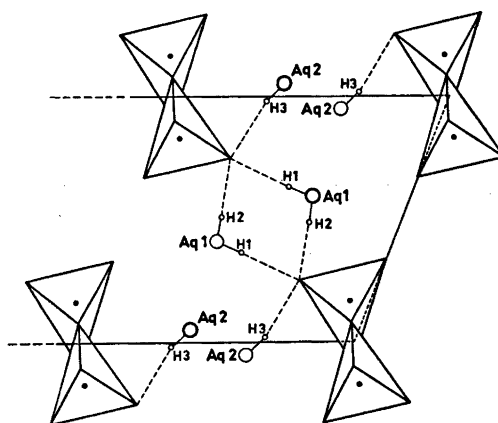

Fig. 3. A projection along [001] showing the hydrogen bonds from Aq1. The left-hand chain is related to the right-hand chain by a 1/2,0,1 translation. The positions of the vanadium atoms are indicated by black dots.

Fig. 4. A projection along [010] showing the hydrogen bonds. Aq atoms with heavy contours are situated in y~3/4, Aq atoms with light contours are in y~1/4. The positions of the vanadium atoms are indicated by black dots.

Table 4. Hydrogen bond and O − H distances (Å). The designation of the atoms refers to Figs. 3 and 4. The estimated standard deviations are given in parentheses and refer to the last decimal place given.

O − O		O − H	
Aq1 − H1···O2	2.821(2)	Aq1 − H1	0.83(4)
		Aq1 − H2	0.79(4)
Aq1 − H2⟨ O2	3.081(4)	Aq2 − H3	0.88(7)
⟨ O2′	3.165(4)		
Aq2 − H3···O2	2.830(3)		

for hydrogen bonding. Aq1 participates in an ordinary hydrogen bond Aq1 − H1····O2 with bond length 2.821(2) Å, and in what seems to be a bifurcated bond Aq1 − H2⟨$^{O2}_{O2′}$. Aq2 is less tightly bonded to the vanadate oxygen atoms with only one atom (O2) within hydrogen bond distance. However, every Aq2 atom has another two Aq2's at distances of 2.622(4) Å. This suggests hydrogen bonds, but as described above, it has not been possible to determine the position of the hydrogen atom. It seems highly probable that it should be located close to a line Aq2 − Aq2′.

Since Aq2 is bonded to the vanadate chains *via* one hydrogen atom only, this could be the explanation of why Aq2 alone accounts for the nonstoichiometry of the crystal.[20]

Hydrogen bonds are shown in Figs. 3 and 4, and hydrogen bond distances are given in Table 4.

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