X-Ray Structural Characterization of the Protonation Sites in the Dihydrogenhexaniobate Anion

Tomoji OZEKI, Toshihiro YAMASE,* Haruo NARUKE,*,† and Yoshinori SASAKI†
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227
†Department of Applied Chemistry, Faculty of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263
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Direct evidence for the locations of the hydrogen atoms in the dihydrogenhexaniobate anion has been obtained by a single-crystal X-ray diffraction method. Hexasodium dihydrogenhexaniobate icosahydrate (**1**), $Na_6[H_2Nb_6O_{19}]\cdot 20H_2O$, crystallizes in triclinic form, space group $P\bar{1}$, $a=10.364(2)$, $b=12.205(2)$, $c=9.026(2)$ Å, $\alpha=103.21(2)$, $\beta=111.10(2)$, $\gamma=109.27(2)°$, $V=924.0(5)$ Å^3, $Z=1$. The hexaniobate anion in **1** is protonated at two bridging oxygen atoms with the O–H distance of 0.69(6) Å. Due to the protonation and interactions with the Na^+ counter-cations, the point symmetry of the hexaniobate anion is reduced to C_{2h} from its possible highest symmetry of O_h.

As a multivalent anion, every polyoxometalate can potentially undergo multi-step protonation in solution depending on the acidity of its environment as is demonstrated by equilibrium studies in aqueous solutions.[1] In the solid state, the protons in the polyoxometalate crystals are important in defining the crystal packing through hydrogen bonds. However, direct measurements of the hydrogen atoms in the polyoxometalate crystals have been limited to those in $[H_2W_{12}O_{42}]^{10-}$ by neutron diffraction[2] and in $[H_2V_2I_2O_{16}]^{6-}$ and $[H_3V_{10}O_{28}]^{3-}$ by X-ray diffraction.[3,4] In many cases their locations have only been predicted from the analyses of metal–oxygen bond lengths,[5] or even left undetermined. The protonation sites in the polyoxometalates are important in that protons will be attached to the most basic oxygen atoms, which are also expected to provide the binding sites for the attachment of the cationic groups to the polyoxometalate surface. The most basic oxygen atoms in the hexaniobate anion have been expected to be the bridging oxygen atoms because the cationic moieties are attached to the bridging oxygen atoms in the $[\{Eu_3O(OH)_3(OH_2)_3\}_2Al_2(Nb_6O_{19})_5]^{26-}$ and $[Mn(Nb_6O_{19})_2]^{12-}$ anions.[6,7] Although various magnitudes of protonation were observed for the hexaniobate anion in aqueous solution[8,9] and in the solid state,[9,10] the only crystal structure analysis of the hexaniobate anion was done for the monohydrogen heptasodium salt, where the proton was found not to be attached to the hexaniobate anion but to form a H_3O^+ cation.[11,12] Here we report the first structural investigation on a protonated hexaniobate anion, which found that the protonation occurs at the bridging oxygen atoms.

Experimental

Compound **1** was obtained as a colorless crystalline byproduct from the preparative procedure for $Na_x H_{26-x}[\{Tb_3O(OH)_3(OH_2)_3\}_2Al_2(Nb_6O_{19})_5]\cdot nH_2O$ (**2**).[6] A 0.345-g sample of Tb_4O_7 was dissolved in a minimum amount (about 1.0 mL) of concentrated HNO_3 by heating almost to the boiling point, then 0.60 g of $[H_2edta]Na_2\cdot 2H_2O$ was added to the solution, the pH of which was then brought to 10—11 with concentrated NaOH aqueous solution. This solution was added dropwise to 60 mL of an aqueous solution dissolving 1.2 g of $Na_7H[Nb_6O_{19}]\cdot 15H_2O$[7] at 353 K with vigorous agitation. A 10 mL aqueous solution of 0.90 g $Al(NO_3)_3\cdot 9H_2O$ the pH of which was adjusted at 10—11 was added to the mixture, which was then concentrated to 50 mL by heating. The solution was cooled to 273 K with ice until a white powder precipitated. The precipitate was collected by filtering and was dissolved by heating in a minimum amount of water. The solution was filtered again and the filtrate was kept at room temperature, from which a mixture of the colorless crystals of compounds **1** and **2** was obtained.

A single crystal of **1** with the dimensions of 0.2×0.2×0.1 mm was mounted on a Rigaku AFC5S four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.71069$ Å). The lattice parameters were obtained from the least-squares of the 2θ values of 25 carefully centered reflections with $20°<2\theta<25°$. The crystal data are as follows: triclinic, space group $P\bar{1}$, $a=10.364(2)$, $b=12.205(2)$, $c=9.026(2)$ Å, $\alpha=103.21(2)$, $\beta=111.10(2)$, $\gamma=109.27(2)°$, $V=924.0(5)$ Å^3, F.W.=1361.7, $Z=1$, $D_{calcd}=2.45$ g cm^{-3}, $F(000)=666$, $\mu(Mo\,K\alpha)=19.88$ cm^{-1}. A total of 5718 reflections was collected with 2θ ranging from 5 to 60°, of which 4058 independent reflections with $I_{obsd}>3\sigma(I_{obsd})$ were used for the structure determination. The ω–2θ scan mode was used for data collection; $\Delta\omega=(1.0+0.35\tan\theta)°$; scan speed 4° min^{-1} in ω. The range of indices was $-13\leq h\leq 14$, $-16\leq k\leq 17$, $-12\leq l\leq 0$, $(\sin\theta/\lambda)_{max}=0.70$ Å^{-1}. Lorentz-polarization and absorption corrections based on four ψ scan curves[13] [transmission factors 0.942—1.000] were applied. Three standard reflections monitored every 100 reflections showed intensity variations within ±1.0% in F_{obsd}. Locations of the Nb atoms were found by the direct method using SHELXS86.[14] Succeeding least-squares and difference Fourier calculations located the Na and O atoms. With all these atoms in anisotropic mode, full-matrix least-squares refinement converged to $R=0.043$ and $wR=0.044$ for 232 variables. At this point, two of the ten O atoms of water molecules of crystallization, O16 and O17, showed extremely skewed thermal ellipsoids and a considerable amount of electron density was found about 1.3 Å from each, suggesting that each should split into two sites. The original atoms

were designated a and those from the difference Fourier map were designated b. Site occupancy factors (sof) for these atoms were refined with the constraint that sof(O16a) = sof(O17a) = 1 − sof(O16b) = 1 − sof(17b). With O16a and O17a anisotropic and O16b and O17b isotropic modes, full-matrix least-squares converged to $R=0.037$ and $wR=0.041$ for 241 variables. Difference Fourier synthesis with the refined parameters showed well-defined peaks attributable to a hydrogen atom attached to O5, a bridging O atom of the hexaniobate anion, and all the hydrogen atoms of water molecules of crystallization except for those were disordered. They showed lower height than the ripples around the Nb atoms, but were clearly distinguishable and geometrically reasonable to be assigned as hydrogen atoms. The positional and the isotropic thermal parameters were refined for H5, the hydrogen atom that was directly bonded to O5. Positional parameters for the other H atoms were fixed at the peak-tops in the difference Fourier map and their B_{iso} values were fixed at 4.0 Å^2. These parameters were not refined but included in the structure factor calculations. Full-matrix least-squares refinement on F finally converged to $R=0.034$ and $wR=0.036$ for 245 variables and 4058 observations. The site occupancy factor for O16a and O17a converged to 0.741(8). The function minimized was $\sum w(|F_{obsd}|-|F_{calcd}|)^2$. The weighting scheme used was $w^{-1}=\sigma^2(F_{obsd})+(0.005|F_{obsd}|)^2$. $S=[\{\sum w(|F_{obsd}|-|F_{calcd}|)^2\}/(n-m)]^{1/2}=1.63$. $(\Delta/\sigma)_{max}=0.009$. The maximum positive and negative peaks in the final difference Fourier map were 1.64 and −0.96 e/Å^3, respectively. Neutral atom scattering factors for non-hydrogen atoms were taken from Cromer and Waber;[15] scattering factors for hydrogen atoms from Stewart, Davidson, and Simpson;[16] anomalous dispersion parameters from Creagh and McAuley;[17] and mass attenuation coefficients from Creagh and Hubbell.[18] All the calculations were done using the TEXSAN[19] software package. Final atomic parameters are listed in Table 1.[20]

Table 1. Positional Parameters and Equivalent Isotropic or Isotropic Thermal Parameters (Å^2) for the Non-Hydrogen Atoms and the Proton of the Anion in **1**

Atom	x	y	z	B_{eq}[a]/B_{iso}
Nb1	0.58770(5)	0.34809(4)	0.52083(6)	0.990[b]
Nb2	0.39207(5)	0.41117(4)	0.18863(5)	1.006
Nb3	0.75022(5)	0.64748(4)	0.55265(6)	1.004
Na1	0.7450(3)	0.4089(2)	0.2555(3)	2.05
Na2	0.6402(3)	0.1204(2)	−0.0114(3)	2.83
Na3	0.7887(3)	0.1397(2)	−0.2935(3)	2.64
O1	0.6572(4)	0.2338(3)	0.5284(4)	1.53
O2	0.3348(4)	0.3563(3)	−0.0359(4)	1.64
O3	0.9266(4)	0.7524(3)	0.5711(4)	1.56
O4	0.4957(4)	0.3124(3)	0.2651(4)	1.17
O5	0.6257(4)	0.5476(3)	0.2765(4)	1.21
O6	0.7692(4)	0.4915(3)	0.5410(4)	1.14
O7	0.3725(4)	0.2609(3)	0.4816(4)	1.15
O8	0.6494(4)	0.4420(3)	0.7645(4)	1.23
O9	0.2132(4)	0.3130(3)	0.2095(4)	1.29
O10	0.5000	0.5000	0.5000	1.03
O11	0.9670(5)	0.5088(5)	0.2414(6)	3.73
O12	0.7776(4)	0.2317(4)	0.2901(5)	2.23
O13	0.5979(5)	0.3003(4)	−0.0481(5)	2.33
O14	0.3938(5)	0.0801(4)	0.0025(5)	2.85
O15	0.5475(5)	0.0272(4)	−0.3028(5)	2.28
O16a[c]	0.8965(7)	0.2617(7)	0.0006(8)	3.91
O16b[c]	0.942(3)	0.364(2)	−0.040(3)	6.0(7)
O17a[c]	0.858(1)	−0.0133(8)	−0.141(1)	6.03
O17b[c]	0.896(2)	0.119(2)	−0.019(3)	4.5(5)
O18	1.0281(5)	0.2251(4)	−0.2889(5)	3.42
O19	0.7243(5)	−0.0427(4)	−0.5278(6)	3.18
O20	0.8888(5)	0.9854(4)	0.2800(6)	3.29
H5	0.622(8)	0.572(6)	0.214(8)	3(2)

a) $B_{eq}=(8/3)\pi^2\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$. b) O16b, O17b, and H5 were refined isotropically. Anisotropic thermal parameters were refined for all the other non-hydrogen atoms. c) Site occupancy factors for O16a and O17a are 0.741(8) and those for O16b and O17b are 0.259.

Results and Discussion

Although no chemical analyses could be used on compound **1** because it was obtained as a mixture with compound **2**, the X-ray structure analysis unambiguously suggests it should be formulated as $Na_6[H_2Nb_6O_{19}]\cdot 20H_2O$. This formula is equivalent to that reported as $Na_2O\cdot Nb_2O\cdot 7H_2O$ by Balke and Smith.[21] They reported its crystal data to be $a:b:c=0.9559:1.0:0.8394$, $\alpha=71°21'$, $\beta=105°30'$, $\gamma=54°7'$. With the transformation matrix of $(111/010/\bar{1}00)$, the unit cell of **1** is transformed to $a=11.690(4)$, $b=12.205(5)$, $c=10.364(2)$ Å, $\alpha=70.74(3)$, $\beta=105.32(3)$, $\gamma=54.90(3)°$. The face angles observed by Balke and Smith agree with the calculated values using these parameters within 0.84°. Thus compound **1** is concluded to be identical with their $Na_2O\cdot Nb_2O\cdot 7H_2O$. Muller and Rohmer[9] postulated its formula to be $Na_6[H_2Nb_6O_{19}(2H_2O)]\cdot 18H_2O$ based on the conductometric and thermogravimetric analyses.

The unit cell of **1** is composed of a discrete dihydrogenhexaniobate anion, six Na^+ cations, and 20 water molecules of crystallization. In Table 2 are listed the interatomic distances. Figure 1 shows an ORTEP[22] drawing of the dihydrogenhexaniobate anion and the coordination spheres of the Na^+ cations. O1 through O10 are the O atoms in the $[H_2Nb_6O_{19}]^{6-}$ anion. O11 through O20 are the O atoms of the water molecules of crystallization, of which O11 through O19 coordinate to Na^+ cations while O20 does not coordinate to any metal atoms. O16 and O17 are disordered: O16 splits into O16a and O16b, and O17 splits into O17a and O17b. Refinement with only O16a and O17a led to poorer R factors and extremely anisotropic thermal parameters with large B_{eq} (11.3—13.3 Å^2) values for these atoms. Distances among these atoms are 1.70(2) Å for O16a–O16b, 1.70(2) Å for O16a–O17b, and 1.57(2) Å for O17a–O17b. O···O contacts from these O atoms to the other O atoms are no less than 2.86 Å. Therefore the site occupancy factors of these atoms were refined based on the following assumption: O16a and O17a make a group that exists simultaneously, and O16b and O17b make another group which exists simultaneously

Table 2. Selected Interatomic Distances (Å) in **1**[a)]

Atom	Atom	Distance	Atom	Atom	Distance
Nb1	Nb2	3.3766(7)	Nb1	$Nb2^i$	3.3510(9)
Nb1	Nb3	3.3738(7)	Nb1	$Nb3^i$	3.3432(9)
Nb2	Nb3	3.5658(10)	Nb2	$Nb3^i$	3.2690(7)
Nb1	O1	1.772(3)	Nb1	O8	1.977(3)
Nb1	O7	1.982(3)	Nb1	O6	2.017(3)
Nb1	O4	2.027(3)	Nb1	O10	2.3339(5)
Nb2	O2	1.777(3)	Nb2	O4	1.946(3)
Nb2	O9	1.949(3)	Nb2	$O8^i$	1.966(3)
Nb2	O5	2.149(4)	Nb2	O10	2.4224(6)
Nb3	O3	1.775(3)	Nb3	$O7^i$	1.944(3)
Nb3	$O9^i$	1.950(3)	Nb3	O6	1.961(3)
Nb3	O5	2.150(4)	Nb3	O10	2.4151(6)
Na1	O11	2.287(5)	Na1	O13	2.364(4)
Na1	O12	2.367(4)	Na1	O5	2.415(4)
Na1	O6	2.429(4)	Na1	O4	2.504(4)
Na2	O15	2.286(4)	Na2	O12	2.350(4)
Na2	$O14^{ii}$	2.379(5)	Na2	O13	2.447(5)
Na2	O14	2.492(5)	Na2	O16a	2.593(7)
Na2	O17b	2.68(2)			
Na3	O18	2.334(5)	Na3	O16a	2.339(6)
Na3	O15	2.381(4)	Na3	O19	2.393(5)
Na3	O17b	2.43(2)	Na3	$O1^{iii}$	2.462(4)
Na3	O16b	2.63(2)	Na3	O17a	2.690(8)

a) See Fig. 1 for the notations of the symmetry codes.

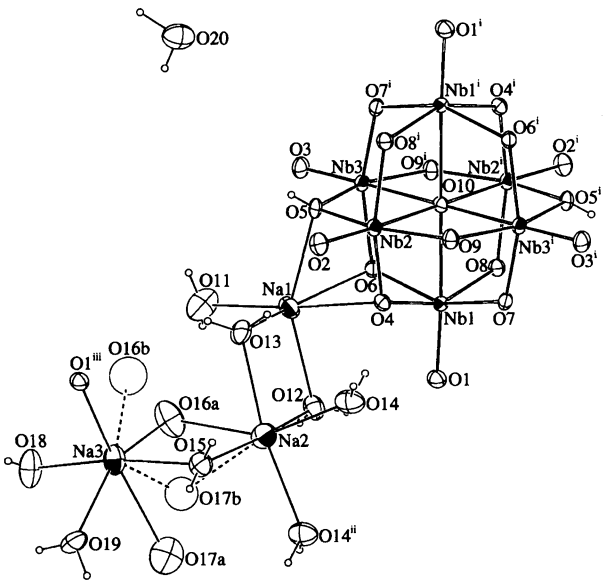

Fig. 1. ORTEP drawing of the $[H_2Nb_6O_{19}]^{6-}$ anion and the coordination spheres of the Na^+ cations. Bonds to the less-occupied water molecules (O16b and O17b) are shown in dotted lines. Thermal ellipsoids are scaled to enclose the 50% probability levels. Hydrogen atoms are shown in open circles with 0.1 Å diameter. Symmetry codes are as follows: (i) $1-x$, $1-y$ $1-z$; (ii) $1-x$, $-y$, $-z$; (iii) x, y, $-1+z$.

when O16a and O17a do not exist. All the Na^+ cations achieve distorted octahedral coordination whether the group a or the group b exists.

The $[H_2Nb_6O_{19}]^{6-}$ anion, located at the crystallographic inversion center at (1/2 1/2 1/2), has the same metal–oxygen framework as the parent Lindqvist-type $[Nb_6O_{19}]^{8-}$ anion.[11,12] It consists of an octahedrally packed array of six NbO_6 octahedra sharing edges. Six NbO_6 octahedra share one O atom, O10, in common at the center of symmetry with the Nb–O distances of 2.3339—2.4224 Å. Each NbO_6 octahedron has a terminal O atom, O1 through O3, with the Nb–O distances of 1.772—1.777 Å *trans* to the central O10 atom. The remaining O atoms, O4 through O9, are bonded to two Nb atoms, of which O5 is protonated by H5 with the O–H distance of 0.69(6) Å. The location of H5 was deduced from a well-defined peak in the difference Fourier map. Its positional and thermal parameters were refined and converged to reasonable values. According to the equilibrium studies,[8,9] this proton is labile and will be neutralized in more basic conditions. All the Nb–O distances except for two for the doubly bridging O atoms are in the range 1.944—2.027 Å, which are comparable to the Nb–O distances of 1.970—2.055 Å for the doubly bridging O atoms in $Na_7(H_3O)[Nb_6O_{19}]\cdot 14H_2O$.[12] The exceptions are the bonds to O5, the protonated O atom: 2.149 Å for Nb2–O5 and 2.150 Å for Nb3–O5. This elongation of the Nb–O bonds is explained by the reduction of the electron density at O5 due to the attachment of a proton to it. The sums of Nb–O bond and Na–O bond valences[23] at O4–O9 are in the range 1.70—1.82 except 1.24 for O5. As a result of the elongations of the bonds Nb2–O5 and Nb3–O5, the distance between Nb2 and Nb3 is elongated to 3.5658 Å. The Nb2–$Nb3^i$ distance is in turn shortened to 3.2690 Å (See Fig. 1 for the symmetry codes). Nb1–Nb2 and Nb1–Nb3 distances are 3.3766 and 3.3738 Å while Nb1–$Nb2^i$ and Nb1– $Nb3^i$ distances are 3.3510 and 3.3432 Å. This is because the former Nb–Nb pairs are bridged by O4 and O6, the O atoms coordinating to the Na1 atom. The O atoms bridging the latter Nb–Nb pairs do not coordinate to any Na^+ cations and these Nb–Nb distances agree well with those of 3.316—3.356 Å found in $Na_7(H_3O)[Nb_6O_{19}]\cdot 14H_2O$.[12] The attachment of the cationic moieties to the $[Nb_6O_{19}]^{8-}$ groups in the $[\{Eu_3O(OH)_3(OH_2)_3\}_2Al_2(Nb_6O_{19})_5]^{26-}$ and $[Mn(Nb_6O_{19})_2]^{12-}$ anions also resulted in the elongation of the Nb–O and Nb–Nb distances.[6,7] As a result of this deformation originating in the protonation and the coordination to the Na^+ cations, the point symmetry of the $[H_2Nb_6O_{19}]^{6-}$ anion was reduced to C_{2h} from its possible highest symmetry of O_h, which was observed for the $[Nb_6O_{19}]^{8-}$ anion in $Na_7(H_3O)$-$[Nb_6O_{19}]\cdot 14H_2O$.[12] The acidic proton bonded to O5 clearly illustrates that the bridging O atom is more basic than the terminal O atoms in the hexaniobate anion. In the decavanadate anion, $[V_{10}O_{28}]^{6-}$, which has a similar metal–oxygen framework structure, the X-ray diffraction analyses showed that the protonation occurs at the bridging oxygen atoms.[4,5]

As shown in Fig. 2, the O5–H5 bond is directed to

Table 3. Geometry of the Hydrogen Bonds in **1**[a)]

	O–H···O		O–H distance/Å	H···O distance/Å	O–H···O angle/°	O···O distance/Å
O5	H5	$O2^{iv}$	0.69(6)	2.11(6)	165(7)	2.783(5)
O11	H11a	$O6^{v}$	0.82	1.92	170	2.733(5)
O11	H11b	$O16b^{vi}$	0.79	2.38	121	2.86(2)
O11	H11b	$O18^{vi}$	0.79	2.41	160	3.159(7)
O12	H12a	O1	0.76	2.16	151	2.848(5)
O12	H12b	$O3^{v}$	0.70	2.09	170	2.781(5)
O13	H13a	$O8^{iii}$	0.84	1.95	158	2.742(5)
O13	H13b	O2	0.99	2.14	153	3.055(5)
O14	H14a	$O20^{iv}$	0.86	1.98	161	2.805(6)
O14	H14b	O4	0.89	1.94	167	2.814(5)
O15	H15a	$O1^{ii}$	0.68	2.33	140	2.874(5)
O15	H15b	$O19^{viii}$	0.85	1.94	168	2.773(6)
O18	H18a	$O2^{vii}$	0.85	1.92	172	2.761(5)
O18	H18b	$O3^{vi}$	0.54	2.30	158	2.807(5)
O19	H19a	$O7^{ii}$	0.87	1.94	146	2.705(5)
O19	H19b	$O20^{ix}$	0.82	2.03	168	2.837(6)
O20	H20a	$O18^{vi}$	0.81	2.27	146	2.975(7)
O20	H20b	$O3^{x}$	1.10	1.99	127	2.802(5)

a) Symmetry codes are as follows: (i)—(iii) same as those in Fig. 1; (iv) $1-x$, $1-y$, $-z$; (v) $2-x$, $1-y$, $1-z$; (vi) $2-x$, $1-y$, $-z$; (vii) $1+x$, y, z; (viii) $1-x$, $-y$, $-1-z$; (ix) x, $-1+y$, $-1+z$; (x) $2-x$, $2-y$, $1-z$.

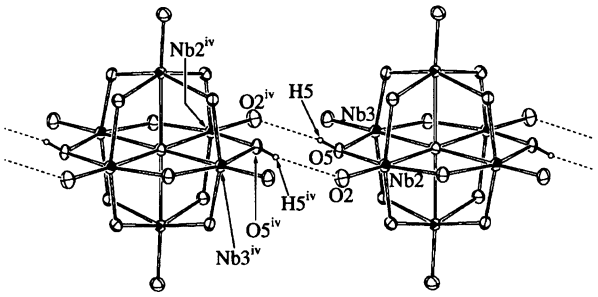

Fig. 2. Perspective view of the hydrogen-bonded chain of $[H_2Nb_6O_{19}]^{6-}$ anions in the crystal of **1**. See Table 3 for the symmetry code.

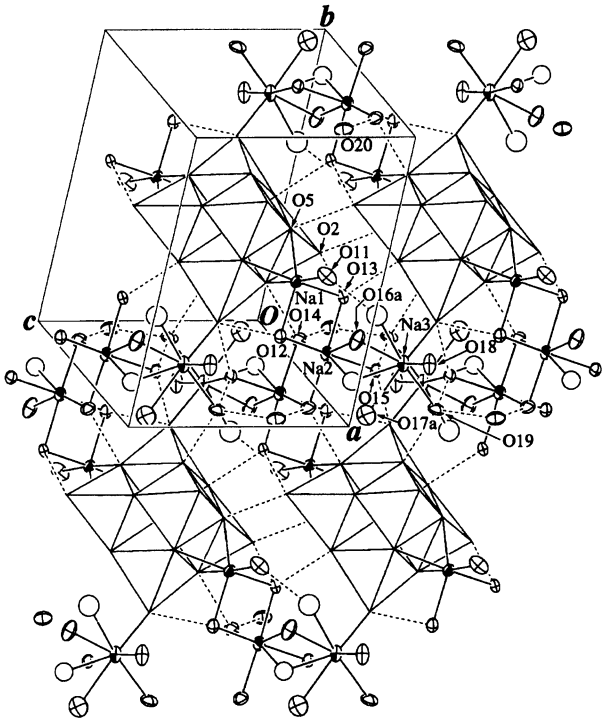

Fig. 3. Packing diagram of **1** viewed down the a^* axis. The $[H_2Nb_6O_{19}]^{6-}$ anions are shown in the polyhedral representations and H atoms are not shown for clarity. Hydrogen bonded O···O contacts are shown with dotted lines.

a terminal O atom, $O2^{iv}$, of the anion in the next cell, forming a O5–H5···$O2^{iv}$ hydrogen bond with the donor O5–H5 distance of 0.69(6) Å, receptor H5···$O2^{iv}$ distance of 2.11(6) Å and O5···$O2^{iv}$ distance of 2.783(5) Å. $H5^{iv}$ in the next cell is interacting with O2 in the original cell. Thus the two $[H_2Nb_6O_{19}]^{6-}$ amions, related to each other by the inversion center at (1/2, 1/2, 0), form a centrosymmetric doubly hydrogen-bonded pair, the geometry of which is similar to that found in the $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H)]_2^{4-}$ dimer.[24)] However, compound **1** forms hydrogen-bonded one-dimensional infinite chains along the crystallographic c axis while $[(\eta^5-C_5H_5)Ti(W_5O_{18}H)]_2{}^{4-}$, $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)Cl]_2{}^{4-}$, and $[H_3V_{10}O_{28}]_2{}^{6-}$ form hydrogen-bonded discrete dimers.[24,4)]

Figure 3 shows the packing diagram of **1**. Between the hydrogen bonded $[(H_2Nb_6O_{19})^{6-}]_\infty$ chains are the hydrated Na^+ cations, each of which achieves octahedral coordination by the O atoms of the hexaniobate anions and/or water molecules of crystallization. They link the $[(H_2Nb_6O_{19})^{6-}]_\infty$ chains to extend the two-dimensional hydrogen- and ionic-bonded layers of $[H_2Nb_6O_{19}]^{6-}$ anions and NaO_6 octahedra parallel to

the *bc* plane of the crystal. Hydrogen-bonds involving the water molecules of crystallization link these layers to build up the three-dimensional crystal packing. The hydrogen- and ionic-bond network defines the orientation of the $[H_2Nb_6O_{19}]^{6-}$ anion and prevents orientational disorder, which would make the identification of the protonation sites more difficult. In Table 3 are listed the geometry of hydrogen bonds in **1**. The donor O–H distances, receptor H···O distances, and O···O contacts are in the range 0.54—1.10, 1.92—2.41, and 2.705—3.159 Å and the O–H···O angles are in the range 121—172°, which are classified as the weak hydrogen bonds according to the Brown's[25] classification. To our knowledge, this is the third example of the complete characterization of the hydrogen bond network in a polyoxometalate crystal: The precedents are the X-ray analysis on $Na_6[H_2V_2I_2O_{16}]\cdot 10H_2O$[3] and the neutron diffraction work on $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$.[26] While 14 of 34 N–H···O hydrogen bonds were three-centered in the latter, only one of 17 is three-centered in **1** and all the hydrogen bonds are two-centered in $Na_6[H_2V_2I_2O_{16}]\cdot 10H_2O$. This is because the hydrogen-bond donors are the water molecules the donor ability of which is much less than those of the NH_4^+ donor.

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