Neutron diffraction structure of $Y_2V_{10}O_{28} \cdot 24H_2O$ at 297 and 60 K

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The structure of yttrium-decavanadate-24-hydrate, $[Y_2V_{10}O_{28} \cdot 24H_2O]$, was determined by neutron diffraction at temperatures of 297 and 60 K. Space group *P*-1, triclinic, $Z = 2$; at 297 K : $a = 9.36(1)$, $b = 9.86(1)$, $c = 23.53(3)$ Å, $\alpha = 98.79(2)$, $\beta = 98.15(2)$, $\gamma = 89.30(2)$, $V = 2123(5)$; at 60 K : $a = 9.19(3)$, $b = 9.85(3)$, $c = 23.31(12)$ Å, $\alpha = 99.03(3)$, $\beta = 98.99(6)$, $\gamma = 89.39(6)°$, $V = 2058(13)$. Final *R* factors of 10 and 9.4% were obtained using 1955 and 1100 observed structure factors at both temperatures, respectively. The position of the 24 water molecules was determined and the characteristics of the hydrogen bonds were analyzed at both temperatures.

KEY WORDS: Yttrium-decavanadate; neutron diffraction; hydrogen bonds.

Introduction

The decavanadate anion, $[V_{10}O_{28}]^{6-}$, is the most condensed polyoxoanion found in vanadium (V) chemistry and consists in a stacking of 10 VO_6 octahedra. Six of such octahedra generate a compact rectangular 2×3 arrangement in which they shared O—O edges. Two additional octahedra are located above and the other two below this rectangle. This seems to be the largest stacked-octahedral isopolyanion cluster compatible with metal—metal repulsion.[1]

The structural characteristics of this cluster are well known from X-ray structural studies of deca-vanadates with inorganic and organic cations.[2–20] Its vibrational spectroscopic behavior has also been investigated and some of its salts present a very inter-

esting thermal behavior, as different intermediate or final pyrolysis products can be stabilized.[21–27] In most of the known structures the polyoxoanion presents a distorted mmm symmetry. Previous crystallographic studies of $Y_2V_{10}O_{28} \cdot 24H_2O$[5,7] suggested that in this compound the intrinsic symmetry deviates more than in other decavanadates, but retaining its inversion center. As departures from mmm symmetry could be due to strong hydrogen bonds connecting the hydrated cation and the polyanions, we have reinvestigated $Y_2V_{10}O_{28} \cdot 24H_2O$ by neutron diffraction at temperatures 297 and 60 K to determine the configuration of the water molecules and the characteristics of the H-bond nets.

Experimental section

$Y_2V_{10}O_{28} \cdot 24H_2O$ was obtained following the procedure of Jahr and Preuss.[28] Single crystals of sufficient dimensions to the study by neutron diffraction were grown by the hanging seed method, by spontaneous concentration of saturated aqueous solutions of $Y_2V_{10}O_{28}$ kept in a thermostat at room temperature.

Details concerning the crystal data, data collection, and refinement conditions for 297 and 60 K structures are given in Table 1. The low temperature

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Table 1. Crystal Data, Data Collection, and Refinements Conditions

		Crystal data	
Chemical formula		$H_{48}O_{52}V_{10}Y_2$	
CCDC no.	1003/5924		1003/5925
Temperature (K)	297		60
F000		368	
D_c(g cm^{-3})		2.453	
Crystal system		triclinic	
Space group		P-1	
a(Å)	9.36(1)		9.19(3)
b(Å)	9.86(1)		9.85(3)
c(Å)	23.53(3)		23.31(12)
α(°)	98.79(2)		99.03(6)
β(°)	98.15(2)		98.99(6)
γ(°)	89.30(2)		89.39(4)
V(Å^3)	2123(5)		2058(13)
No. reflections for refinements of lattice parameters	25 ($34 < 2\theta < 45°$)		21 ($34 < 2\theta < 52°$)
Radiation		Orphée reactor, CEN Saclay	
Wavelength λ(Å)	1.531(5)		1.526(5)
		$\lambda/2$ contamination $< 1.9 \times 10^{-4}$	
Absorption coefficient μ(cm^{-1})		4.16 (measured)	
Crystal color		Orange	
Crystal size (mm)		$3.0 \times 2.0 \times 0.3$	
Crystal description	Parallelepiped	$< -7\,11\,0><1\,2\,2>$ and $<1\,-2\,8>$	
		Data collection	
Diffractometer		Four-circle diffractometer (6T2channel)	
Data collection range and scan mode	ω-scan for $3 < 2\theta < 50°$ ω/θ-scan for $50 < 2\theta < 80$ $\omega/2\theta$-scan for $80 < 2\theta < 140$, 3–5 s/step, 41 steps, adjusted as a function of the scattering angle by $6–8tg\theta + 18tg^2\theta$		ω-scan for $3 < 2\theta < 50$ ω/θ-scan for $50 < 2\theta < 80$ 3–5 s/step, 41 steps, adjusted as a function of the scattering angle by $6–8tg\theta + 18tg^2\theta$
Index range	$-8 < h < 8$ $-9 < k < 9$ $0 < l < 21$		$-7 < h < 7$ $0 < k < 7$ $-19 < l < 17$
No. of reflections measured	3431		1820
R_{int}	0.049		Unique set
No. of independent reflections	2267		1820
No. of reflections with $I > 2\sigma(I)$	1955		1100
Standard reflections variation	$(0\,1\,-9)$ and $(-2\,3\,3)$, constant throughout the data collection period		
	10 days		9 days
Absorption correction type		Numerical methods using crystal shape	
Transmission factors (min, max)		0.2044; 0.8340	
		Refinement	
Refinement method		Full matrix least squares on F^2	
No. of refined parameters	681		406
Weighting scheme		$\omega = 1/\sigma^2(F^2)$	
R for all reflections, and R and R_ω for observed reflections	0.161 0.100 0.093		0.161 0.094 0.115
Goodness of fit all and observed reflections	1.92 1.71		2.24 1.85
Extinction correction method		SHELXL	
Extinction coefficient	0.00268(18)		0.00099(15)
Source of the neutron scattering lengths		*International Tables of Crystallography*[23]	

Table 2. Final Fractional Atomic Coordinates, Occupation Factors, and Thermal Parameters with Estimated Standard Deviations in Parentheses[a]

Atom	x	y	z	Uiso/Ueq	Atom	x	y	z	Uiso/Ueq
	Temperature = 297 K					Temperature = 297 K			
Y1	0.93294	0.02310	0.12355	0.05159	H341*	.13598	.22644	.19277	.07159
Y2	0.37793	0.49569	0.38035	0.05093	H342*	−.00443	.31031	.19113	.08811
V1*	0.48100	0.28300	0.05500	0.01279	O35	.26219	.04993	.9455	.05065
V2*	0.60800	0.27400	0.93900	0.01330	H351*	.34478	−.00987	.95333	.07627
V3*	0.21700	0.47300	0.07800	0.01672	H352*	.3145	.1438	.9534	.06756
V4*	0.33900	0.46100	0.96200	0.01178	O36	.13711	.05913	.08056	.06899
V5*	0.47500	0.46300	0.85000	0.01127	H361*	.1838	.15208	.07565	.07063
V6*	0.93100	0.19500	0.43000	0.01381	H362*	.20184	−.00267	.06993	.09209
V7*	0.14600	0.23500	0.54400	0.01507	O37	.46194	.33622	.30956	.06183
V8*	0.66000	0.01300	0.42300	0.01494	H371*	.56198	.30674	.30756	.07418
V9*	0.87000	0.05300	0.53700	0.01571	H372*	.40797	.29913	.27315	.08153
V10*	0.09700	0.09500	0.64800	0.01659	O38	.34075	.28924	.41848	.05941
O1	0.51862	0.12403	0.04956	0.06070	H381*	.39258	.22072	.41353	.09984
O2	0.29266	0.29134	0.06814	0.05920	H382*	.25477	.24927	.43166	.09378
O3	0.56042	0.34974	0.12949	0.05328	O39	.60066	.42545	.42768	.05088
O4	0.41458	0.28555	0.96842	0.05495	H391*	.64259	.33831	.42415	.07693
O5	0.65740	0.34195	0.02424	0.05219	H392*	.67501	.49287	.44291	.07304
O6	0.44758	0.50313	0.04953	0.05818	O40	.74777	.32887	.66736	.07453
O7	0.64106	0.11633	0.93703	0.06299	H401*	.7877	.25471	.64562	.06494
O8	0.51448	0.28286	0.86661	0.06078	H402*	.77443	.33151	.70577	.05551
O9	0.77857	0.34525	0.92653	0.05842	O41	.81394	.45106	.56625	.04774
O10	0.06205	0.44208	0.09211	0.06481	H411*	.85138	.36666	.54924	.07351
O11	0.33524	0.50551	0.15124	0.05625	H412*	.88663	.52298	.5642	.10745
O12	0.18351	0.43768	0.99010	0.05728	O42	.5552	.31428	.55179	.0573
O13	0.29473	0.43638	0.88884	0.06370	H421*	.45793	.25991	.55269	.06543
O14	0.40513	0.43412	0.78324	0.06219	H422*	.61252	.25554	.53439	.11021
O15	0.96793	0.34463	0.42254	0.07436	O43	.17839	.38703	.3174	.06005
O16	0.73739	0.18729	0.42071	0.05689	H431*	.17165	.29024	.30813	.08031
O17	0.95146	0.09422	0.35911	0.07266	H432*	.08593	.42334	.31751	.06421
O18	0.93586	0.22200	0.51801	0.05462	O44	.44088	.38198	.66008	.06948
O19	0.13597	0.14286	0.46100	0.05448	H441*	.41813	.41276	.69855	.08274
O20	0.09214	0.01825	0.54857	0.05252	H442*	.39532	.31107	.64096	.0964
O21	0.18153	0.38797	0.53372	0.06914	O45	.32239	.25872	.20375	.07218
O22	0.11903	0.25600	0.61881	0.06231	H451*	.37895	.16698	.18813	.09408
O23	0.33450	0.16764	0.55936	0.06263	H452*	.33795	.33314	.18105	.09759
O24	0.08380	0.14808	0.71489	0.06676	O46	.48587	.03055	.17428	.06055
O25	0.28876	0.05333	0.64926	0.05593	H461*	.44808	−.02422	.13887	.12423
O26	0.49027	0.03754	0.40804	0.07737	H462*	.47738	−.02825	.20391	.1138
O27	0.69489	0.07043	0.50979	0.05918	O47	.07194	.51706	.80182	.06621
O28	0.88595	0.10744	0.61031	0.05514	H471*	.14052	.49175	.82841	.10683
O29	0.01152	0.19329	0.92523	0.06445	H472*	.10367	.5021	.76452	.07158
H291*	0.08522	0.25593	0.94799	0.08137	O48	.84376	.32581	.78247	.06602
H292*	−0.07845	0.24329	0.92385	0.07813	H481*	.9268	.38489	.7909	.08223
O30	0.20038	0.13308	0.83152	0.06478	H482*	.77217	.37094	.80611	.07534
H301*	0.27204	0.19453	0.84785	0.11718	O49	.19923	.08818	.29934	.07974
H302*	0.16813	0.15515	0.79456	0.08465	H491*	.11862	.08078	.3256	.15037
O31	0.90188	0.05818	0.80713	0.06355	H492*	.27844	.04428	.31229	.12432
H311*	0.88577	0.15117	0.80314	0.08031	O50	.73679	.24904	.29439	.09399
H312*	0.86550	−0.00218	0.76956	0.06779	H501*	.74945	.21714	.25088	.12425
O32	0.88026	0.20805	0.06985	0.06162	H502*	.79212	.18803	.31486	.10755
H321*	0.79294	0.24765	0.05459	0.05723	O51	.0936	.50631	.68796	.05084
H322*	0.95343	0.28299	0.07859	0.11449	H511*	.15179	.57607	.67924	.09549
O33	0.73857	0.14741	0.16774	0.06125	H512*	.10535	.41294	.66202	.0919
H331*	0.65167	0.09100	0.17086	0.06407	O52	.52645	.10714	.73443	.10722
H332*	0.70425	0.22998	0.15381	0.07789	H521*	.44995	.08887	.70386	.12841
O34	0.03724	0.21528	0.18538	0.05995	H522*	.52848	.19101	.74748	.21467

Table 2. Continued

Atom	x	y	z	Uiso	Atom	x	y	z	Uiso
	Temperature = 60 K					Temperature = 60 K			
Y1	.93578	.02772	.12432	.02159	H341	.13955	.22821	.19343	.01296
Y2	.38273	.48403	.38046	.02843	H342	−.00194	.30542	.19139	.02514
V1	.48100	.28300	.05500	.00384	O35	.26234	.05124	.94582	.02271
V2	.60800	.27400	.93900	.00399	H351	.34590	−.01035	.95455	.03566
V3	.21700	.47300	.07800	.00502	H352	.31280	.14316	.95611	.03454
V4	.33900	.46100	.96200	.00343	O36	.14418	.06112	.08149	.01281
V5	.47500	.46300	.85000	.00338	H361	.18808	.14996	.07932	.02836
V6	.93100	.19500	.43000	.00414	H362	.20065	−.00931	.06621	.03211
V7	.14600	.23500	.54400	.00452	O37	.47573	.32169	.31307	.00516
V8	.66000	.01300	.42300	.00448	H371	.57064	.30865	.30913	.04854
V9	.87000	.05300	.53700	.00471	H372	.41856	.29777	.27581	.01581
V10	.09700	.09500	.64800	.00498	O38	.34166	.27863	.42287	.00991
O1	.51675	.12157	.05047	.02059	H381	.39693	.19944	.41083	.03538
O2	.29120	.29116	.06879	.02356	H382	.26506	.24376	.43572	.04152
O3	.56721	.35564	.13010	.02012	O39	.60780	.41319	.43536	.01010
O4	.40876	.28796	.96664	.02248	H391	.64660	.32779	.42043	.03774
O5	.66182	.33785	.02512	.02107	H392	.67454	.48433	.44764	.02013
O6	.44507	.50004	.04892	.02157	O40	.73494	.33061	.66358	.02042
O7	.63713	.11251	.93658	.01942	H401	.76535	.25727	.63892	.01804
O8	.50424	.28387	.86456	.01264	H402	.76666	.33332	.70365	.02985
O9	.77492	.34544	.92447	.01192	O41	.81531	.46492	.56723	.01010
O10	.05813	.45224	.09453	.01555	H411	.83848	.36873	.54278	.05311
O11	.33657	.50445	.15379	.02470	H412	.88888	.52267	.56718	.03804
O12	.17934	.44680	.99121	.00979	O42	.54324	.33453	.54483	.01000
O13	.28449	.44612	.88667	.01907	H421	.47429	.26297	.54270	.03754
O14	.39708	.43334	.77823	.02586	H422	.56286	.34474	.50983	.03815
O15	.96901	.34343	.42083	.01914	O43	.18815	.38492	.31536	.01297
O16	.73376	.17633	.41532	.01340	H431	.18262	.28357	.30495	.03100
O17	.95646	.08989	.35795	.00499	H432	.09103	.42125	.31471	.03155
O18	.92392	.22490	.51478	.02720	O44	.43093	.39903	.65986	.01101
O19	.13392	.14387	.46392	.02999	H441	.40780	.41396	.69391	.01606
O20	.08869	.02004	.55113	.01383	H442	.39284	.32177	.63902	.04494
O21	.17779	.38989	.53426	.02003	O45	.33514	.25940	.20364	.02319
O22	.10865	.26186	.62026	.02187	H451	.38694	.18185	.18475	.03841
O23	.33225	.17066	.56232	.02213	H452	.35095	.33157	.18446	.02829
O24	.07240	.16223	.71575	.03658	O46	.48211	.03480	.17082	.02615
O25	.29036	.06583	.65528	.02828	H461	.44494	.98780	.13572	.02611
O26	.48337	.02956	.39814	.02005	H462	.46703	.97258	.19972	.06165
O27	.68435	.06086	.50674	.02170	O47	.06224	.51635	.80031	.02008
O28	.87059	.11000	.60885	.01373	H471	.13962	.49754	.83199	.04403
O29	.00967	.19274	.92455	.02221	H472	.09394	.49665	.76469	.05368
H291	.07442	.25489	.94666	.03223	O48	.83083	.32596	.77959	.01797
H292	−.07975	.24340	.92361	.04759	H481	.92032	.38729	.78961	.04451
O30	.20255	.12697	.83229	.00884	H482	.76599	.37728	.80043	.01903
H301	.28997	.18046	.84525	.03866	O49	.20060	.08871	.30179	.01840
H302	.16636	.15953	.79398	.10471	H491	.13240	.07817	.32665	.02945
O31	.89120	.05453	.80438	.01634	H492	.28919	.05077	.31090	.08842
H311	.87865	.15686	.80121	.04296	O50	.75221	.25203	.29029	.02925
H312	.86455	.00220	.76875	.02638	H501	.75872	.21364	.25262	.03544
O32	.88555	.21587	.06986	.02552	H502	.81016	.18074	.31612	.03572
H321	.79252	.24307	.05293	.04048	O51	.07972	.50755	.68443	.01436
H322	.95290	.28506	.08140	.04384	H511	.14982	.57507	.68391	.05880
O33	.73614	.14688	.16657	.02222	H512	.08670	.42667	.65983	.02273
H331	.65572	.09942	.16960	.01876	O52	.52211	.11107	.74119	.02979
H332	.69818	.22848	.15533	.06621	H521	.44047	.09172	.71390	.02583
O34	.04106	.21034	.18557	.02765	H522	.52245	.20118	.76154	.08706

$^a U_{eq} = 1/3\ \Sigma U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$, starred atoms were refined isotropically.

was attained cooling the specimen with a cooling rate of 3 K/min within a closed-cycle refrigerator. The observed diminution of the cell volume at 60 K (3%) is essentially due to the contraction of the **a** and **c** cell parameters; **b** remains constant within experimental error.

For both structures, the oxygen of water molecules were located from difference Fourier map phased with the X-ray positions and isotropic thermal parameters of all the atoms not belonging to water molecules, previously refined with neutron diffraction data. Subsequent difference maps gave the positions of the missing hydrogen atoms. The small dimension of the crystal limited the neutron diffraction. Moreover, the number of collected intensities for the structure at 60 K was further reduced because of the cooling experimental conditions. As a consequence vanadium and hydrogen atoms of the 297 K structure were refined isotropically and all other atoms were refined anisotropically. In the case of the 60 K structure, the positions of vanadium atoms were fixed to those of the 297 K structure and its isotropic thermal parameters were estimated. This can be justified by the weak neutron scattering length of the vanadium. The other atoms were refined with isotropic thermal parameters. In the last difference maps the absolute value of the largest residual peak was smaller than 14.2% and 25.9% of the peak height of a removed oxygen atom used as a reference, to 297 and 60 K structures, respectively.

Structure refinement was performed with the SHELXL93 program[29] on a Hewlett-Packard Vectra VA PC. Final atomic parameters are presented in Table 2.

Results and discussion

Crystal packing

The crystallographic symmetry generates two independent decavanadate polyanions in the lattice. The crystal cell also contains four hydrated yttrium cations. Figure 1 shows a stereoscopic view of the crystal packing. This may be described as built from layers, parallel to the (0 0 1) plane, which contain all the ions. In these layers, the $[V_{10}O_{28}]^{6-}$ polyanions are joined to the $[Y(H_2O)_8]^{3+}$ cations *via* hydrogen bridges formed by the water molecules coordinated to the Y(III) ions. The water molecules not coordinated to cations are located between layers, the generated
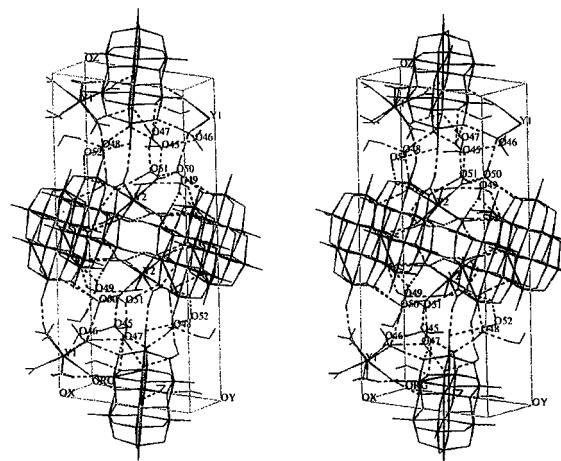
Fig. 1. Stereoscopic view of structural packing of Y$_2$V$_{10}$O$_{28}$.24H$_2$O crystal (for clarity, only water molecules of class 2 and class 1′ were labeled).

hydrogen bridges involving these atoms join the layers along the [0 0 1] direction.

Anions and cations

Selected bond distances concerning the independent units $[Y(H_2O)_8]^{3+}$ and $[V_{10}O_{28}]^{6-}$ at 297 and 60 K are presented in Table 3. In this crystallographic study the coordination distances and angles of vanadium and yttrium atoms are less dispersed than those in the X-ray structure.[5,7,8]

No appreciable geometrical differences are observed between the two independent $[V_{10}O_{28}]^{6-}$ units, the superposition of both polyhedra *via* a least-squares procedure gives a root mean square (rms) deviation of less than 0.04 Å. For the $[Y(H_2O)_8]^{3+}$ cations, the superposition of the two independent units shows small distortions (rms 0.16 Å). In this case the largest observed distance (0.21 Å) between corresponding atoms after superposition occurs for the two pairs O30—O37 and O33—O44; this difference may be correlated with the different hydrogen bond strength associated to the corresponding water molecules (Table 3).

$[V_{10}O_{28}]^{6-}$ is a discrete unit of 10 distorted VO$_6$ octahedra (bond angles at the V atoms ranging from 74 to 107°) joined by a common side (Fig. 2). The two independent polyanions are located around the crystallographic centers of inversion at $\frac{1}{2}, \frac{1}{2}, 0$ and $0, 0, \frac{1}{2}$ and describe a pseudo body-centered arrangement. The V—O distances, which depend upon the type of oxo ligand, vary between (distance in Å):

Table 3. Selected Bond Distances (Å) and Angles at 297 K Temperature (First Column, esd on Distances 0.02 Å, on Angles 1°) and at 60 K (Second Column, esd on Distances 0.03 Å, on Angles 1°) Concerning the Two Crystallographic Independents Units of:

$[Y(H_2O)_8]^{3+}$ cations[a]							
A1	A2	d_{295}	d_{60}	A1	A2	d_{295}	d_{60}
Y_1	O29[i]	2.35	2.38	Y_1	O33	2.45	2.42
Y_1	O30[i]	2.44	2.43	Y_1	O4[iii]	2.34	2.24
Y_1	O31[ii]	2.31	2.35	Y1	O35[i]	2.31	2.30
Y_1	O32	2.38	2.41	Y_1	O36[iii]	2.34	2.34
Y_2	O37	2.33	2.32	Y_2	O41[iv]	2.34	2.35
Y_2	O38	2.39	2.45	Y_2	O42[iv]	2.30	2.32
Y_2	O39	2.37	2.42	Y_2	O43	2.37	2.28
Y_2	O40[iv]	2.41	2.40	Y_2	O44[iv]	2.47	2.46

$[V_{10}O_{28}]^{6-}$ polyanions[b]						
V1	O1	O2	O3	O5	O4[i]	O6
O1	1.59 1.61	2.71 2.69	2.68 2.72	2.71 2.72	2.74 2.80	3.79 3.79
O2	104 103	1.83 1.82	2.73 2.74	3.76 3.76	2.75 2.76	2.68 2.65
O3	103 104	96 97	1.83 1.84	2.75	3.80 3.82	2.69
O5	96 97	157 158	91 89	2.02 2.01	2.48	2.59
O4[i]	97 98	91 90	157 155	75 76	2.05 2.07	2.63 2.59
O6	170 172	83 82	83 82	75 77	76 75	2.21 2.18
V2	O7	O9	O8	O5[ii]	O4	O6[iii]
O7	1.58 1.61	2.67 2.71	2.66 2.71	2.78 2.77	2.79 2.81	3.81 3.86
O9	103 105	1.83 1.80	2.69 2.68	2.71 2.72	3.75 3.72	2.65 2.61
O8	103 103	95 94	1.82 1.86	3.72 3.75	2.69 2.66	2.65 2.68
O5[ii]	101 100	90 92	154 154	2.01 1.99	2.48 2.52	2.59 2.61
O4	101 101	154 153	89 86	76 77	2.02 2.03	2.63 2.59
O6[iii]	174 174	81 79	81 81	74 75	75 74	2.24 2.26
V3	O10	O9[iii]	O2	O11	O12[i]	O6
O10	1.58 1.59	2.71	2.68 2.74	2.76 2.72	2.79 2.80	3.96 3.92
O9[iii]	106 103	1.81 1.80	3.62 3.61	2.62	3.94 3.87	2.65 2.61
O2	100 103	153 154	1.91 1.90	2.64 2.64	2.60 2.63	2.68 2.65
O11	105 102	90 89	88 88	1.90 1.91	3.82 3.80	2.74 2.77
O12[i]	101 103	88 87	83 86	153 155	2.02 1.97	2.70 2.61
O6	175 177	77 77	76 77	79 81	75 74	2.38 2.33
V4	O12	O13	O4	O5[iii]	O6[ii]	O6[iii]
O12	1.71 1.73	2.73 2.76	2.68 2.69	2.74 2.70	2.70 2.61	3.78 3.78
O13	107 106	1.70 1.73	2.68 2.72	2.75 2.71	3.81 3.80	2.74 2.71
O4	96 98	97 100	1.88 1.83	2.48 2.52	2.63 2.60	2.58 2.59
O5[iii]	98 94	99 94	155 158	1.92 1.96	2.57 2.61	2.59 2.61
O6[ii]	88 86	166 168	81 83	80 80	2.15 2.09	2.64
O6[iii]	165 164	88 90	81 83	78 80	77 78	2.09 2.09
V5	O14	O11[iii]	O3[iii]	O8	O13	O6[iii]
O14	1.60 1.70	2.71 2.72	2.71 2.72	2.72 2.73	2.82 2.86	3.94 4.02
O11[iii]	105 103	1.81 1.78	2.65 2.64	2.65 2.69	3.79 3.80	2.74 2.75
O3[iii]	103 101	92 94	1.87 1.83	3.72 3.59	2.64 2.51	2.69 2.65
O8	102 101	91 95	154 154	1.90 1.86	2.60	2.65 2.68
O13	100 98	155 159	84 80	82 83	2.07 2.08	2.66 2.71
O6[iii]	174 174	82 84	78 78	77 79	74 75	2.35 2.34

Table 3. Continued

V6	O15	O16	O17	O18	O19^{iv}	O20^{v}
O15	1.56 1.56	2.66 2.71	2.68 2.69	2.76 2.73	2.71 2.69	3.80 3.80
O16	105 107	1.80 1.80	2.71 2.68	2.72 2.66	3.75 3.70	2.69 2.65
O17	104 102	96 94	1.84 1.88	3.78 3.75	2.73 2.72	2.67 2.62
O18	99 101	90 90	154 155	2.04 1.96	2.50 2.48	2.60 2.68
O19^{iv}	96 98	156 154	90 89	76 78	2.04 2.00	2.64 2.57
O20^{v}	171 172	82 81	81 78	75 78	76 74	2.26 2.25
V7	O21	O23	O22	O19	O18^{vi}	O20
O21	1.61 1.61	2.69	2.68 2.69	2.74 2.70	2.79 2.79	3.83 3.84
O23	100 102	1.88 1.83	2.68 2.70	2.74 2.68	3.77 3.80	2.68 2.65
O22	104 102	93 95	1.79 1.84	3.74 3.70	2.70 2.74	2.65 2.65
O19	98 99	89 91	158 157	2.01 1.93	2.50 2.48	2.64 2.62
O18^{vi}	102 99	156 157	91 89	78 77	1.97 2.05	2.60 2.68
O20	174 176	81 81	82 81	77 78	76 77	2.22 2.23
V8	O26	O16	O23^{v}	O27	O25^{v}	O20^{v}
O26	1.60 1.65	2.71 2.67	2.72 2.76	2.83 2.87	2.70 2.68	3.95 3.97
O16	102 102	1.88 1.80	3.68 3.61	2.62 2.67	2.67 2.67	2.69 2.65
O23^{v}	102 102	155 156	1.89 1.89	2.64 2.57	2.63 2.62	2.68 2.65
O27	102 107	84 92	85 85	2.02 1.91	3.78 3.83	2.64 2.70
O25^{v}	102 94	91 90	89 85	155 158	1.85 1.99	2.77 2.79
O20^{v}	176 175	78 79	78 77	74 79	81 80	2.35 2.33
V9	O28	O27	O19^{v}	O18	O20^{iv}	O20^{v}
O28	1.71 1.70	2.73 2.69	2.76 2.79	2.69 2.73	2.64 2.65	3.79 3.82
O27	107 103	1.69 1.75	2.73 2.71	2.69 2.71	3.75 3.73	2.64 2.70
O19^{v}	98 101	97 95	1.94 1.94	2.50 2.45	2.64 2.62	2.64 2.57
O18	96 98	96 95	157 157	1.92 1.94	2.60 2.68	2.63 2.64
O20^{iv}	87 91	166 165	82 81	81 85	2.09 2.02	2.64 2.65
O20^{v}	165 170	88 87	81 79	81 80	82 79	2.11 2.16
V10	O24	O25	O22	O17^{v}	O28^{vi}	O20
O24	1.60 1.66	2.70 2.71	2.70 2.64	2.73 2.78	2.84 2.84	3.94 3.90
O25	103 104	1.83 1.78	2.66 2.68	2.66 2.70	3.80 3.88	2.77 2.79
O22	103 97	92 94	1.85 1.87	3.65 3.65	2.61 2.62	2.65 2.65
O17^{v}	102 104	91 95	154 155	1.90 1.87	2.61 2.65	2.67 2.62
O28^{vi}	101 96	155 161	84 81	83 82	2.06 2.15	2.64 2.65
O20	174 169	82 87	77 79	77 78	74 74	2.35 2.25

^{a}Symmetry codes: (i) $-x+1, -y, -z+1$. (ii) $x, y, z-1$. (iii) $x+1, y, z$. (iv) $-x+1, -y+1, -z+1$.
^{b}Symmetry codes: (i) $x, y, z-1$. (ii) $x, y, z+1$. (iii) $-x+1, -y+1, -z+1$. (iv) $x+1, y, z$. (v) $-x+1, -y, -z+1$.
  (vi) $x-1, y, z$.

— to V=O$_t$ (O$_1$, O$_7$, O$_{10}$, O$_{14}$ and O$_{15}$, O$_{21}$, O$_{24}$, O$_{26}$; oxo terminal, oxygen atoms bonded to only one vanadium atom)

$(1.58\text{–}1.60)_{297K}$ $(1.59\text{–}1.70)_{60K}$ and $(1.56\text{–}1.61)_{297K}$ $(1.56\text{–}1.66)_{60K}$

— to V—O$_{2b}$ (O$_2$, O$_3$, O$_8$, O$_9$, O$_{11}$, O$_{12}$, O$_{13}$, and O$_{16}$, O$_{17}$, O$_{22}$, O$_{23}$, O$_{25}$, O$_{28}$, O$_{27}$; oxygen atoms shared between two vanadium atoms)

$(1.70\text{–}2.07)_{297K}$ $(1.73\text{–}2.08)_{60K}$ and $(1.69\text{–}2.06)_{297K}$ $(1.70\text{–}2.15)_{60K}$

— to V—O$_{3b}$ (O$_4$, O$_5$, and O$_{18}$, O$_{19}$; oxygen atoms shared between three vanadium atoms)

Table 3. Water Molecules

O	H	C	O–H	O–C	H–O–H	C–O–H	C–O–C	H–H	A	H–A	O–H–A	O–A
					Class 1: one bond to the bisector of the lone pairs							
O29		Y1[i]		2.35 2.38	106 101			1.56 1.43				
	H291		0.97 0.90			122 127			O12	2.07 2.17	160 155	3.00 3.04
	H292		0.97 0.96			131 132			O9[iv]	1.67 1.66	160 174	2.63 2.62
O30		Y1[i]		2.43 2.43	106 101			1.48 1.50				
	H301		0.91 0.95			130 135			O8	2.40 2.18	155 171	3.25 3.12
									O13	2.43 2.65	140 122	3.16 3.25
	H302		0.94 1.00			123 124			O24	1.92 1.90	164 161	2.83 2.86
O31		Y1[ii]		2.32 2.35	110 110			1.60 1.59				
	H311		0.94 1.03			126 124			O48	1.88 1.85	171 167	2.82 2.86
	H312		1.00 0.91			121 120			O49[i]	1.74 1.76	173 175	2.74 2.67
O32		Y1		2.38 2.41	106 114			1.55 1.55				
	H321		0.95 0.94			133 127			O5	1.70 1.63	169 161	2.64 2.54
	H322		0.99 0.91			115 113			O10[iii]	1.84 1.88	170 166	2.82 2.77
O33		Y1		2.44 2.42	108 104			1.59 1.44				
	H331		1.01 0.90			116 120			O46	1.67 1.73	167 169	2.68 2.62
	H332		0.96 0.93			118 122			O3	1.87 1.83	154 161	2.76 2.73
O34		Y1[iv]		2.34 2.24	106 103			1.54 1.50				
	H341		0.92 0.91			121 125			O45	1.75 1.80	175 176	2.67 2.71
	H342		1.01 1.01			127 126			O47[v]	1.80 1.83	176 174	2.81 2.83
O35		Y1[i]		2.20 2.30	100 101			1.54 1.54				
	H351		0.98 0.99			121 120			O1[i]	1.69 1.68	167 165	2.66 2.64
	H352		1.03 1.00			128 131			O4	1.66 1.65	174 173	2.68 2.65
O36		Y1[iv]		2.35 2.34	103 110			1.52 1.56				
	H361		1.05 0.98			129 126			O2	1.76 1.76	169 169	2.80 2.73
	H362		0.87 0.92			127 124			O7[i]	1.85 1.80	168 156	2.72 2.67
O37		Y2		2.33 2.32	106 108			1.55 1.49				
	H371		0.98 0.90			128 127			O50	1.78 1.85	173 169	2.76 2.73
	H372		0.95 0.94			126 118			O45	1.70 1.72	170 172	2.65 2.66
O38		Y2		2.39 2.45	101 104			1.43 1.46				
	H381		0.83 0.96			123 116			O26	2.01 1.85	169 168	2.83 2.79
	H382		1.01 0.90			133 135			O19	1.81 1.82	164 169	2.79 2.71
O39		Y2		2.37 2.41	109 116	129 117	110	1.54 1.58				
	H422		2.06			119 112						
	H391		0.94 0.95			93			O16	1.72 1.68	174 163	2.65 2.60
	H392		0.96 0.92			107			O21[vi]	1.77 1.80	176 172	2.72 2.71
O40		Y2[vi]		2.41 2.40	112 117			1.52 1.58				
	H401		0.93 0.92			120 118			O28	1.86 1.84	173 163	2.79 2.73
	H402		0.90 0.91			127 125			O48	1.84 1.79	174 176	2.74 2.72
O41		Y2[vi]		2.34 2.35	106 108			1.56 1.58				
	H411		0.95 1.06			133 128			O18	1.74 1.70	174 164	2.69 2.74
	H412		1.00 0.89			120 125			O15[vii]	1.86 1.83	168 170	2.84 2.70
O42		Y2[vi]		2.30 2.32				1.57 1.52				
	H421		1.07 0.94			121 130			O23	1.52 1.76	161 158	2.58 2.66
	H422		0.88		112	115			O27	2.06	168	2.93
	H422		0.88		107	135			O39	2.01	156	2.83
O43		Y2		2.37 2.23	109 110			1.53 1.59				
	H431		0.95 0.99			121 120			O49	1.99 1.91	168 167	2.92 2.89
	H432		0.93 0.96			121 122			O51[viii]	1.81 1.71	176 178	2.74 2.67
O44		Y2[vi]		2.47 2.46	117 113			1.55 1.44				
	H441		0.96 0.84			121 129			O14	1.99 1.96	164 168	2.93 2.79
	H442		0.85 0.88			122 117			O23	2.21 2.14	151 157	2.99 2.98
									O22	2.61 2.64	131 124	3.23 3.21
									O25	2.78 2.80	144 140	3.51 3.52
					Class 2: two bond to the lone pairs (tetrahedral arrangement)[b]							
O45		H341		1.75 1.80	110 105	110 112	119 115					
		H372		1.70 1.72		106 108						
	H451		1.08 0.98			102 108			1.70 1.51	O46	1.69 1.70	170 164	2.76 2.65

Table 3. Continued

O	H	C	O–H	O–C	H–O–H	C–O–H	C–O–C	H–H	A	H–A	O–H–A	O–A
	H452		0.99 0.92			110 109			O11	1.93 1.94	164 164	2.90 2.84
									O2	2.60 2.63	121 118	3.22 3.17
									O3	2.57 2.55	124 126	3.23 3.17
O46		H331		1.67 1.73	104 105	111 111	108 101					
		H451		1.67 1.70		117 120						
	H461		0.95 0.90			110 110		1.52 1.51	O7^i	1.95 1.87	173 178	2.89 2.76
	H462		0.98 1.01			104 109			O52^i	1.75 1.70	170 166	2.73 2.69
O47		H342^v		1.80 1.83	110 111	121 114	113 116					
		H481^{iv}		1.86 1.79		105 108						
	H471		0.89 0.98			106 109		1.51 1.56	O13	2.01 1.82	180 174	2.90 2.80
	H472		0.96 0.91			101 99			O51	1.80 1.88	157 153	2.70 2.72
O48		H311		1.88 1.85	106 101	112 109	117 118					
		H402		1.84 1.79		109 116						
	H481		0.96 1.00			105 104		1.55 1.49	O47^{iii}	1.86 1.79	172 170	2.81 2.78
	H482		0.99 0.92			108 106			O11^{vii}	1.84 1.81	165 171	2.81 2.73
O49		H312^i		1.74 1.76	110 115	107 109	114 112					
		H431		1.99 1.92		107 103						
	H491		1.05 0.93			90 97		1.60 1.55	O17^{iv}	1.84 1.87	165 160	2.87 2.77
									O28^i	2.57 2.57	123 127	3.26 3.22
	H492		0.89 0.90			127 121			O26	2.79 2.52	143 141	3.55 3.27
									O52	2.60 2.65	136 139	3.31 3.38
O50		H371		1.78 1.85	105 104	116 119	100 96					
		H511^{vii}		1.99 1.90		125 116						
	H501		1.05 0.91			107 115		1.57 1.57	O33	1.96 1.99	170 169	3.00 2.89
	H502		0.93 1.08			102 107			O17	2.01 1.84	166 163	2.91 2.89
									O25	2.79 2.82	130 130	3.46 3.61
O51		H432^v	3.46 3.61	1.81 1.71	112 116	104 110	93 90					
		H472		1.80 1.88		116 118						
	H511		0.95 0.93			113 103		1.65 1.57	O50^{vi}	1.99 1.90	149 155	2.85 2.78
	H512		1.04 0.91			116 116			O22	1.73 1.76	178 173	2.77 2.67
					Class 1′: one bond to one of the lone pairs.							
O52		H462^{vi}		1.75 1.70	109 112							
	H521		0.94 0.93			98 115		1.45 1.53	O25	1.84 1.77	174 173	2.77 2.67
	H522		0.84 0.91			130 98			O8	2.83 2.44	121 130	3.48 3.13
									O14	2.71 2.55	154 149	3.34 3.39

Symmetry codes: (i) $-x+1,-y, -z+1$. (ii) $-x+2, -y, -z+1$. (iii) $x+1$, y, z. (iv) $x-1$, y, z. (v) $-x, -y+1, -z+1$. (vi) $-x+1,-y+1, -z+1$. (vii) $-x+2, -y+1, -z+1$ (viii) $-x, -y+1, -z+1$.

$(1.88–2.05)_{297K}$ $(1.83–2.07)_{60K}$ and $(1.92–2.04)_{297K}$ $(1.93–2.05)_{60K}$

— to V—O$_{6b}$ (O$_6$ and O$_{20}$; oxygen atoms shared between six vanadium atoms)

$(2.09–2.35)_{297K}$ $(2.09–2.34)_{60K}$ and $(2.09–2.35)_{297K}$ $(2.02–2.33)_{60K}$

The V—V distances observed between adjacent VO$_6$ octahedra are in the range :

$(3.07–3.39)_{297K}$ $(3.06–3.41)_{60K}$

These figures show that, at both temperatures, in this yttrium compound the decavanadate polyhedron is basically the same as that in the analo-gous decavanadates of other inorganic and organic cations.

Water structure and hydrogen bonds

Table 3 presents selected distances and angles of the water molecules classified according to the types defined by Ferraris and Franchini-Angela.[32] This table also includes all contacts which could be hydrogen bonds.

The 24 crystallographically inequivalent water molecules occupy C1 sites (no symmetry). At room temperature, 16 are trigonal, coordinated to a single cation (bisector of lone-pairs toward an Yttrium
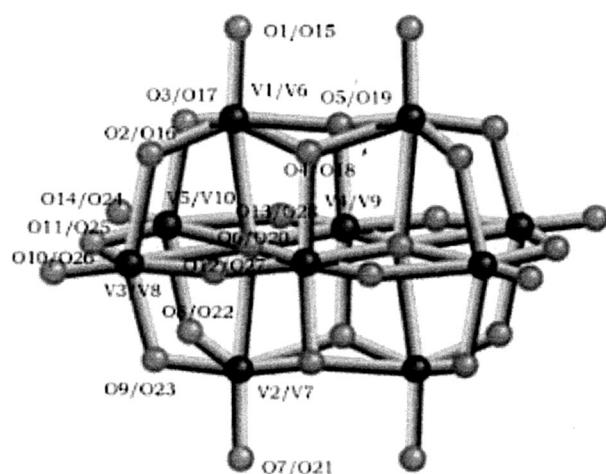
Fig. 2. $[V_{10}O_{28}]^{6-}$ polyanion showing the atom labels of the two independent crystallographic units.

cation), 7 are tetrahedral (lone-pairs toward two H), and the last water molecule W52 could be classified as pyramidal (only one lone-pair accepts a hydrogen bond).

From Table 3 it can be seen that for H442, H452, H502, and H491 there is only one hydrogen bond with its characteristic of directionality, plus two (for H491 and H502) or three (for H442, H452) weak contacts which cannot be considered as real hydrogen bonds according to the criteria of Chiari and Ferraris.[33] At room temperature H301 hydrogen bond clearly splits into two bonds of comparable strength; this bifurcated hydrogen bond is lost at 60 K, the associated distances and angles at this temperature are not of the same order. H492 and H522 have two weak contacts with more or less the same characteristics and a significant shortening of O—H distances; the strength of these interactions is increased at 60 K; they could be classified as bifurcated hydrogen bonds. All other water molecules are donors of two hydrogen bonds.

Between 297 and 60 K, the plane determined by the W42 molecule rotates 60°. At room temperature, H442—O23 hydrogen bond contributes to structural cohesion along the [1 0 0] direction. At 60 K, this hydrogen bond is replaced by H442—O39 which increase the cohesion along [0 0 1] and change the class of the new acceptor atom. W39 water molecule is coordinated, at 60 K, to two atoms and may be classified tetrahedral (class 2).

Conclusion

There is no order/disorder problem in the investigated $Y_2V_{10}O_{28} \cdot 24H_2O$ crystals. Interatomic distances and angles within decavanadate polyhedra show that its geometry is quite similar to that found in other crystalline decavanadates. The positions of the 24 water molecules were determined. Almost all water molecules are donors of two hydrogen bonds. At room temperature W30 presents one bifurcated hydrogen bond which is lost at 60 K. In spite of the multiple contacts observed to H442, H452, H491, and H502, the differences observed in corresponding bond lengths and angles prevent the classification of those as polyfurcated hydrogen bonds. Interaction forces concerning H492 and H522 atoms are increased at 60 K and related bonds could be classified as weak bifurcated hydrogen bonds.

The most outstanding structural change observed in the crystal between 278 and 60 K is a rotation of 60° of W42 molecular plane which alters the hydrogen bond associated system changing one of the acceptor atoms (O27 at 278 K, O39 at 60 K). The coordination of the W39 molecule undergoes variation, from trigonal to tetrahedral.

The present results allow a good insight into the complex net of hydrogen bonds present in this structure and adds interesting structural information to the complex chemistry of condensed vanadium polyanions.

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