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A crystallographic and vibrational study of cesium di-μ-aqua bis[tetraaquasodium(I)] decavanadate, $Cs_4[Na_2(H_2O)_{10}](V_{10}O_{28})$

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The title compound crystallizes in the triclinic space group $P\overline{1}$, with $a = 8.6161(4)$ Å, $b = 10.591(1)$ Å, $c = 11.406(1)$ Å, $\alpha = 67.976(7)^\circ$, $\beta = 86.868(6)^\circ$, $\gamma = 67.798(6)^\circ$, and $Z = 1$. The structure was refined to $R1 = 0.0413$. The decavanadate anion $V_{10}O_{28}{}^{6-}$ and the $[Na_2(H_2O)_{10}]^{2+}$ bridged cation are located at inversion centers. Partial deuteration of the substance indicates that the coordinated water molecules are strongly asymmetric, forming weak hydrogen bonds with acceptor oxygen atoms from the decavanadate anion. The infrared and Raman spectra are dominated by the water and decavanadate anion bands.

KEY WORDS: Decavanadate; cesium; water bridged sodium dimeric group; crystal structure; infrared spectrum; Raman spectrum.

Introduction

During some preparative experiments to obtain the cesium salt of the $VO_2F_2{}^-$ anion, orange colored, crystalline $Cs_4[Na_2(H_2O)_{10}](V_{10}O_{28})$ was obtained. The tetraammonium[1,2] and tetrapotassium[3] salts having the same general formulation are already known. In the ammonium compound the X-ray diffraction study revealed that the sodium atoms are present as a pair of edge-sharing NaO_6 octahedra, each sodium being surrounded by six water molecules, two of which act as bridges between the octahedra. Such crystalline unit was previously found in $Na_2CO_3 \cdot 10\ H_2O$.[4]

The present crystal structure study shows that the $[Na_2(H_2O)_{10}]^{2+}$ cation is also present in the cesium salt. The infrared and Raman spectra of the substance were obtained and interpreted on the basis of the structural study.

Experimental

In a typical preparation procedure, a solution of 0.221 g of $NaVO_3 \cdot H_2O$ in 2 mL of distilled water, to which 15 mL of a 0.5% HF aqueous solution was added, was mixed with a solution of 0.217 g of CsF in 2 mL of water, with the immediate formation of an orange solid. After keeping for 1 h at about 5°C, the solid was filtered and subsequently recrystallized from an aqueous

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solution at room temperature. A mixture of small crystals with different crystal habits, i.e., some opaque, orange prisms and others yellow plates, were obtained. Both kinds of crystals gave identical diffractograms and practically identical infrared and Raman spectra.

A quantitative determination of vanadium by atomic absorption spectrometry gave 29.0%, in agreement with the theoretical 29.7% value. An examination of the crystals using X-ray fluorescence revealed the presence of sodium, vanadium, and cesium.

The crystal data, data collection procedure, structure determination methods, and refinement results are summarized in Table 1. Some of the water H-atoms were found in a difference Fourier map. They were refined employing the riding model with O—H and H · · · H distances restrained to target values of 0.86(1) and 1.40(1) Å, respectively.

The infrared and Raman spectra were run in a FTIR Bruker IFS66 spectrometer, provided with the FRA106 Raman accessory in which light of 1064 nm from a Nd/YAG laser was used for excitation. Pressed disks of the substance mixed with an excess of KBr or powdered polyethylene were used to obtain the infrared spectra, whereas the pure, polycrystalline substance contained in a glass tube served for running the Raman spectra. Deuteration of the substance was attained by recrystallization from H_2O/D_2O mixtures in different proportions.

Crystallographic structural results

Atomic fractional coordinates and equivalent isotropic displacement parameters are given in Table 2. Figure 1 is an ORTEP[9] drawing of the decavanadate anion and the bridged cation.

The decavanadate anion $V_{10}O_{28}{}^{6-}$, is located on a crystallographic inversion center and consists of a discrete unit resulting from the condensation of 10 distorted VO_6 octahedra. Interatomic bond distances and angles within this polyanion are in agreement with previous structural

Table 1. Crystal Data and Structure Solution Methods and Refinement Results for $Cs_4[Na_2(H_2O)_{10}](V_{10}O_{28})$

Empirical formula	$H_{20}Cs_4Na_2O_{38}V_{10}$
CCDC deposit no.	CCDC-1003/6181
Formula weight	1715.18
Temperature, K	293(2)
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions[a]	$a = 8.6161(4)$ Å
	$b = 10.591(1)$ Å
	$c = 11.406(1)$ Å
	$\alpha = 67.976(7)°$
	$\beta = 86.868(6)°$
	$\gamma = 67.798(6)°$
Volume, $Å^3$	888.8(1)
Z, Calculated density, Mg/m^3	1,3.204
Absorption coefficient, mm^{-1}	6.683
$F(000)$	796
Crystal size, mm	0.08 × 0.16 × 0.20
Crystal color/shape	Orange/plate
Diffractometer/scan	Enraf-Nonius CAD-4/ω–2θ
Radiation, graphite monochromator	Cu Kα, $\lambda = 1.54184$ Å
Scan width	$0.8 + 0.35\ \tan\theta$
Standard reflection	(6, 6, 4); (2, −2, −9)
Decay of standard, %	1.5
θ range for data collection, deg	1.94–29.97°
Index ranges	$-12 \leq h \leq 12, -14 \leq k \leq 14, -1 \leq l \leq 16$
Reflections collected/unique	5890/5165 ($R_{\text{int}} = 0.0175$)
Completeness to $\theta = 29.97$, %	100.0
Observed reflections $[I > 2\sigma(I)]$	4104
Data reduction and correction[b]	XCAD4[6]
Structure solution[c] programs	SHELXS97[7]
Refinement[d] programs	SHELXL97[8]
Refinement method	Full-matrix least-squares on F^2
Weights	$w = [\sigma^2(F_o^2) + (0.078P)^2 + 5.71P]^{-1}$, where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$
Data/restraints/parameters	5165/8/262
Goodness of fit on F^2	1.135
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0413$, $wR2 = 0.1179$
R indices (all data)	$R1 = 0.0583$, $wR2 = 0.1259$
Largest diffraction peak and hole, $e/Å^3$	2.33[f] and −2.48[f]

[a] Least-squares refinement of $[(\sin\theta)/\lambda]^2$ values for 25 reflections in the $12.75 < \theta < 27.85°$ range.

[b] Corrections: Lorentz, polarization, and numerical absorption.[5] Maximum and minimum transmission factors of 0.616 and 0.279.

[c] Neutral scattering factors and anomalous dispersion corrections.

[d] Structure solved by Patterson and Fourier methods and the final molecular model obtained by anisotropic full-matrix least-squares refinement of non-hydrogen atoms.

[e] R indices defined as $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

[f] Close to cesium atom positions.

Table 2. Atomic Coordinates (10^4) and Equivalent Isotropic Displacement Parameters (10^3 Å^2) for $Cs_4[Na_2(H_2O)_{10}](V_{10}O_{28})$

Atom	x	y	z	U_{eq}[a]
Cs(1)	1748(1)	1993(1)	4972(1)	24(1)
Cs(2)	2868(1)	−1735(1)	9264(1)	29(1)
V(1)	4705(1)	5049(1)	2635(1)	16(1)
V(2)	6865(1)	5045(1)	4782(1)	13(1)
V(3)	1778(1)	7780(1)	2809(1)	18(1)
V(4)	3805(1)	7768(1)	4967(1)	16(1)
V(5)	5288(1)	7869(1)	2389(1)	17(1)
O(1)	3970(5)	3814(4)	4196(4)	14(1)
O(2)	6797(5)	3889(4)	3847(4)	16(1)
O(3)	4334(5)	6232(4)	3958(4)	14(1)
O(4)	5586(5)	6415(4)	1738(4)	18(1)
O(5)	4994(6)	4078(5)	1772(4)	26(1)
O(6)	2528(5)	6328(4)	2113(4)	18(1)
O(7)	1336(5)	6146(4)	4291(4)	19(1)
O(8)	7354(5)	6340(4)	3575(4)	17(1)
O(9)	1772(5)	8560(4)	4049(4)	19(1)
O(10)	3014(5)	8748(4)	1819(4)	19(1)
O(11)	−126(6)	8721(5)	2160(5)	28(1)
O(12)	4836(5)	8650(4)	3669(4)	18(1)
O(13)	3517(6)	8695(5)	5869(5)	25(1)
O(14)	6085(6)	8918(5)	1390(5)	28(1)
Na	674(4)	3320(3)	1273(3)	31(1)
O(1W)	−2114(7)	5150(6)	139(5)	33(1)
O(2W)	−406(8)	1733(7)	2877(6)	41(1)
O(3W)	3491(7)	1786(5)	2421(6)	36(1)
O(4W)	187(7)	4955(6)	2339(6)	36(1)
O(5W)	951(8)	1714(6)	258(5)	40(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

determinations in other decavanadate salts.[1,10] Selected bond distances for the decavanadate anion appear in Table 3, whereas a complete list of their geometrical parameters is deposited as supplementary material.

The $[Na_2(H_2O)_{10}]^{2+}$ cation is located on another inversion center and consists of two symmetry-related $Na(H_2O)_6$ octahedra, which share the pair of equatorial water ligands defining the octahedra common edge (see Fig. 1). Bond distances and angles within $[Na_2(H_2O)_{10}]^{2+}$ are detailed in Table 4. The Na—Ow bond distances are slightly larger than in the same disodium cation found in the ammonium salt[1] but follow the same general trend, i.e., the shorter bonds are those located in the axes of the NaO_6 octahedra, with a mean value of 2.35 Å (2.34 Å in the NH_4^+ salt), the equatorial terminal bonds follow with 2.42 Å (2.37 Å in the NH_4^+ salt), and the longest are the equatorial bonds forming the bridge, with 2.48 Å (2.43 Å in the NH_4^+ salt). Cis Ow—Na—Ow angles vary from 81.9(2) to 100.2(2)° and trans Ow—Na—Ow angles are in the range 171.6(2)–175.7(2).

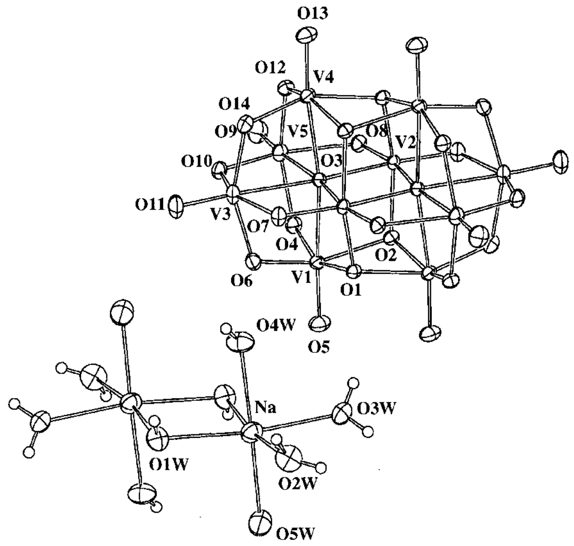

Fig. 1. Molecular plot of the unit cell content of $Cs_4[Na_2(H_2O)_{10}](V_{10}O_{28})$, showing the $V_{10}O_{28}{}^{6-}$ anion and the $[Na_2(H_2O)_{10}]^{2+}$ bridged cation along with the labeling of the non-H atoms and their displacement ellipsoids at the 50% probability level.

The crystal is further stabilized by a net of weak Ow—H···O bonds, where the acceptors are decavanadate oxygen atoms. H-bond distances and angles involving the found hydrogen atoms are given in Table 5.

Spectroscopic results

The infrared and Raman spectra of $Cs_4[Na_2(H_2O)_{10}](V_{10}O_{28})$ are reproduced in Figs. 2–4. Measured wave numbers of the spectral features and their proposed assignment are summarized in Table 6.

Two intense bands centered at 3550 and 3392 cm^{-1} as well as the band at 1625 cm^{-1} in the infrared spectra are due to the stretching

Table 3. Bond Lengths (Å) for the $V_{10}O_{28}{}^{6-}$ Anion in $Cs_4[Na_2(H_2O)_{10}](V_{10}O_{28})$

V1—O1	2.010
V1—O2	1.999
V1—O3	2.238
V1—O4	1.830
V1—O5	1.621
V1—O6	1.818
V2—O1#	1.910
V2—O2	1.917
V2—O3	2.119
V2—O3#	2.097
V2—O7#	1.677
V2—O8	1.706
V3—O3	2.287
V3—O6	1.877
V3—O7	2.057
V3—O9	1.886
V3—O10	1.813
V3—O11	1.605
V4—O3	2.229
V4—O9	1.817
V4—O12	1.817
V4—O13	1.621
V5—O3	2.340
V5—O4	1.878
V5—O8	2.016
V5—O10	1.853
V5—O12	1.888
V5—O14	1.596

Note: Symmetry operation: #: $-x+1, -y+1, -z+1$.

Table 4. Interatomic Bond Distances (Å) and Angles (deg) for $[Na_2(H_2O)_{10}]^{2+}$ in $Cs_4[Na_2(H_2O)_{10}](V_{10}O_{28})^a$

Bond distance	
Na—O(5W)	2.331(7)
Na—O(4W)	2.371(6)
Na—O(2W)	2.393(6)
Na—O(3W)	2.453(6)
Na—O(1W′)	2.471(6)
Na—O(1W)	2.478(6)
Bond angle	
O(5W)—Na—O(4W)	175.7(2)
O(5W)—Na—O(2W)	83.7(2)
O(4W)—Na—O(2W)	93.2(2)
O(5W)—Na—O(3W)	91.4(2)
O(4W)—Na—O(3W)	91.5(2)
O(2W)—Na—O(3W)	88.7(2)
O(5W)—Na—O(1W′)	100.2(2)
O(4W)—Na—O(1W′)	83.2(2)
O(2W)—Na—O(1W′)	171.6(2)
O(3W)—Na—O(1W′)	83.9(2)
O(5W)—Na—O(1W)	95.3(2)
O(4W)—Na—O(1W)	81.9(2)
O(2W)—Na—O(1W)	95.6(2)
O(3W)—Na—O(1W)	172.4(2)
O(1W′)—Na—O(1W)	91.43(19)
Na′—O(1W)—Na)	88.57(19)

[a] Primed atoms are obtained from the unprimed ones through the inversión symmetry operation: $-x, -y+1, -z$.

and bending modes, respectively, of the coordinated water molecules (Fig. 2). The location of the $[Na_2(H_2O)_{10}]^{2+}$ unit in an inversion center means that there are five unique water molecules, related to the other five molecules by the inversion operation. The appearance of two (relatively broad) bands for the water stretching and of a rather narrow band for the water bending indicates that the water molecules are relatively similar in their respective crystallographic environments.

The water molecules are strongly bonded in the $[Na_2(H_2O)_{10}]^{2+}$ unit. In fact, they are not lost after heating the substance at 100°C in vacuum. On the other hand, the relatively high wave numbers of the stretching bands show that these

Table 5. Hydrogen Bonds for $Cs_4[Na_2H_2O)_{10}]V_{10}O_{28})$ with $d(H\cdots A) < r(A) + 2.000$ Å and $\angle(D-H\cdots A) > 110°$

D—H	d(D—H) (Å)	d(H···A) (Å)	∠(D—H···A) (deg)	d(D···A) (Å)	A	Symmetry operation
O1W—H11	0.860	2.066	167.79	2.912	O4	$x-1, y, z$
O2W—H21	0.860	2.147	156.68	2.956	O9	$x, y-1, z$
O2W—H22	0.860	2.267	168.25	3.113	O2	$x-1, y, z$
O2W—H22	0.860	2.560	119.41	3.074	O13	$-x, -y+1, -z+1$
O3W—H31	0.859	2.011	165.46	2.850	O12	$x, y-1, z$
O3W—H32	0.857	2.351	144.15	3.087	O13	$-x+1, -y+1, -z+1$
O3W—H32	0.857	2.373	131.15	3.007	O5	
O4W—H41	0.858	2.072	174.30	2.927	O8	$x-1, y, z$

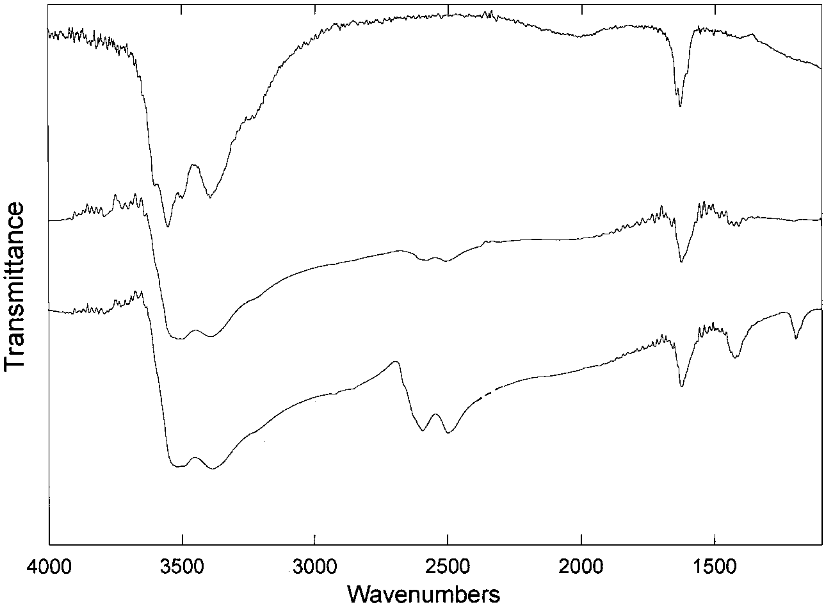

Fig. 2. Infrared spectrum of $Cs_4[Na_2(H_2O)_{10}](V_{10}O_{28})$ in its normal (upper trace) and increasingly deuterated (middle and lower traces) forms, in the water-stretching and water-bending region.

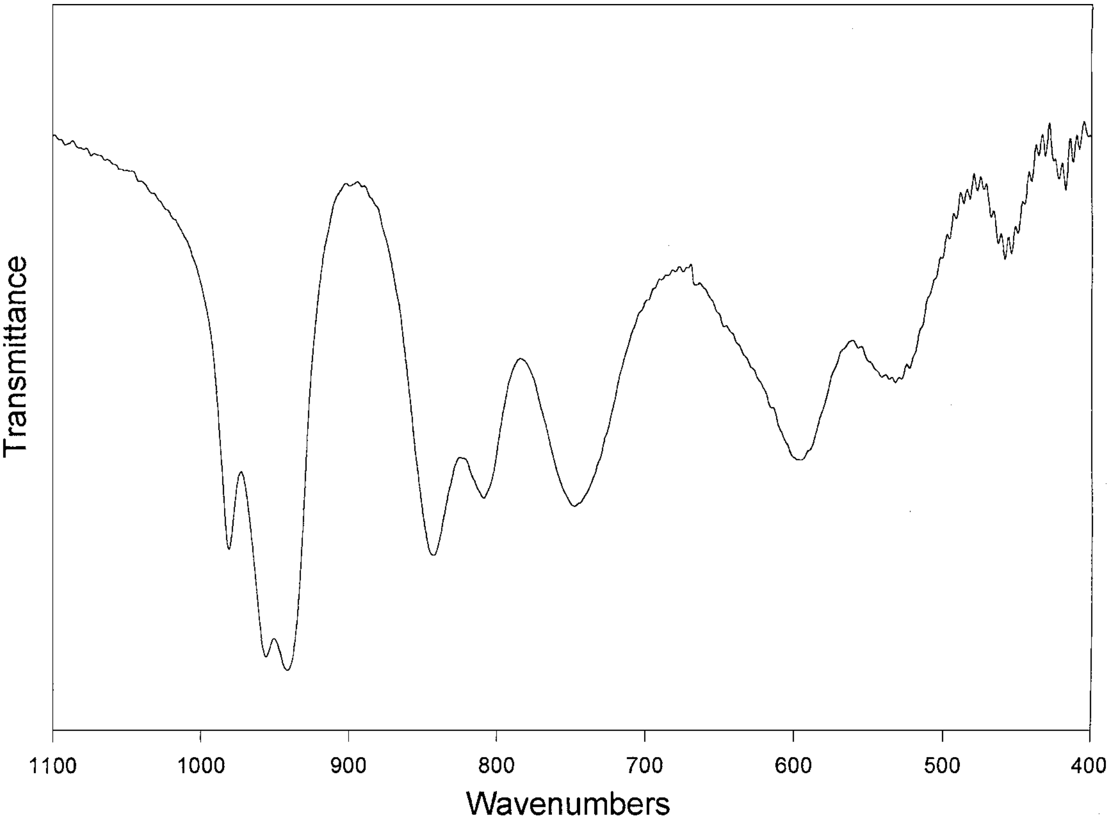

Fig. 3. Infrared spectrum of $Cs_4[Na_2(H_2O)_{10}](V_{10}O_{28})$ in the low wave numbers region.

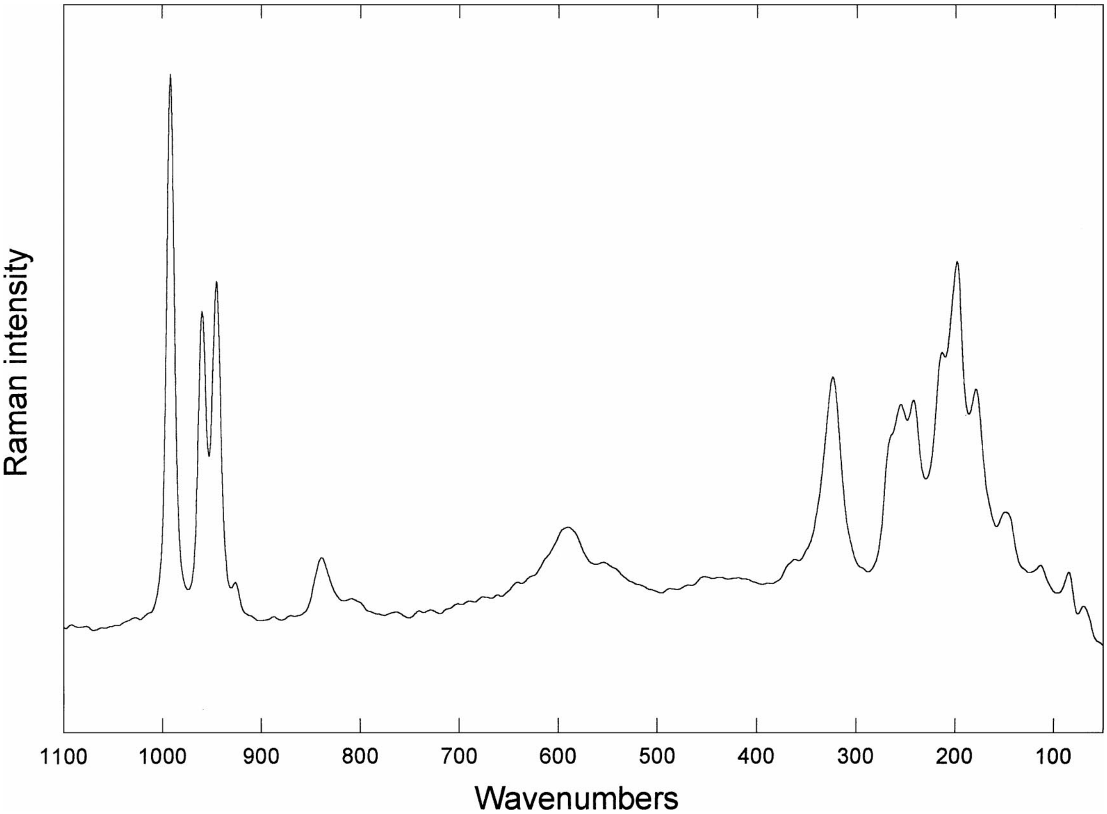

Fig. 4. Raman spectrum of $Cs_4[Na_2(H_2O)_{10}](V_{10}O_{28})$.

molecules are forming weak hydrogen bonds with the surrounding species.[11]

Recrystallization of the substance from mixtures of H_2O and D_2O in different proportions produced partial deuteration, resulting in the appearance of OD stretching bands located at 2593 and 2496 cm^{-1} (Fig. 2) with an isotopic shift of 1.36–1.37, in the range expected for water molecules forming weak hydrogen bonds in crystalline hydrates.[11] Besides, bands due to HOD and D_2O bendings appear at 1421 and 1196 cm^{-1}, respectively. When the deuterium content is substantially diminished, the 1196 cm^{-1} band almost vanishes, but two OD stretching bands still appear, with practically no wave number shift regarding the more deuterated substance. Such bands should be due mainly to HOD species, showing therefore that the water molecules are strongly asymmetric in the crystal lattice (symmetric water molecules with equivalent OH(OD) bonds should originate only one OD stretching band at low deuterium content[11]).

The strongest hydrogen bond is formed between O3W and an oxygen atom from the decavanadate anion acting as acceptor and located at 2.85 Å from the water oxygen, with a $\mathrm{Ow{-}H\cdots O}$ angle of 165.5° (Table 5). Using the known correlations between OD stretching frequencies and $\mathrm{O\cdots O}$ acceptor distances in crystalline deuterated hydrates,[12,13] a wave number of 2510 cm^{-1} is predicted for that bond stretching, in agreement with the observed value of 2496 cm^{-1}. This last value should correspond to the water bond forming the strongest H(D)—bond with the acceptor atom.

Table 6. Wave Numbers of the Observed Bands in the Infrared and Raman Spectra of $Cs_4[Na_2(H_2O)_{10}]$ $(V_{10}O_{28})$ and Their Assignments

Infrared	Raman	Assignments
3550		$\nu(H_2O)$
3496		
3392		$\nu(H_2O)$
3254 sh		$2\delta(H_2O)$
2593		$\nu(HOD)$, $\nu(D_2O)$
2496		$\nu(HOD)$, $\nu(D_2O)$
1625		$\delta(H_2O)$
1610 sh		
1421		$\delta(HOD)$
1196		$\delta(D_2O)$
981	992	$\nu(V{=}O)$
956	960	
940	945	
842	839	$\nu(V{-}O{-}V)$ antisymm.
809		
747		
596	590 br	$\nu(V{-}O{-}V)$ symmetric
531	553	
496		Libration HOD
456		$\nu(V{-}O{-}V)$ symmetric
420		
391	323	$\delta(V{-}O{-}V)$ and $\nu(Na{-}O)$ stretching modes
	254	
230	242	
	213	Decavanadate deformations and $\nu(Na{-}O)$ stretching modes
	199	
171	180	
	148	
	86	

Note: ν, stretching; δ, angular deformation; sh, shoulder; br, broad.

Deuteration of the substance also originates a new band at 496 cm^{-1} and probably a second, weak band at 525 cm^{-1} in the infrared spectrum. Such bands should be due to librational vibrations of HOD or D_2O species.

Bands due to the $V_{10}O_{28}{}^{6-}$ anion appear below 1000 cm^{-1}. An assignment of these bands is given in Table 5, following previous studies made on such anion.[14]

The $[Na_2(H_2O)_{10}]^{2+}$ cation should have Na—O stretching bands mainly in the 200–300 cm^{-1} region, as predicted for the $[Na(H_2O)_n]^+$ ($n = 1$–4) species by means of quantum chemistry calculations.[15] The Raman spectrum of the studied substance shows considerable complexity in the region located below 300 cm^{-1}. Bands due to the mentioned Na—O stretchings and also originating in the angular deformations of the complex anion and cation could appear in that region.

Acknowledgments

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