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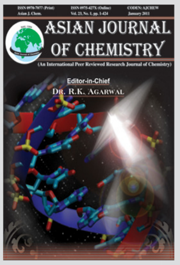

Synthesis and Spectral Characterization of Vanadium Substituted Hexaniobates

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Reaction of aqueous solution of sodium vanadate with potassium niobate at different pH gives three well defined compounds *viz.*, $K_7HNb_3V_3O_{19}\cdot 3H_2O$ (**I**), $K_7HNb_2V_4O_{19}\cdot 5H_2O$ (**II**) and $K_7HNbV_5O_{19}\cdot H_2O$ (**III**). Powder X-ray diffraction analysis shows that the three compounds to be isomorphous with the 'parent' compound, ($K_7HNb_6V_3O_{19}\cdot 15H_2O$) (**IV**). On the basis of IR and Raman spectra, $[Nb_2V_4O_{19}]^{8-}$ is assigned to have *cis*-configuration (C_{2V} symmetry) and $[Nb_3V_3O_{19}]^{8-}$ to have *facial* configuration (C_{3V} symmetry).

Key Words: 6-Polyacids, Synthesis, Vanadium, IR and Raman spectroscopy.

INTRODUCTION

Polyoxometalates have attracted much attention because of their structural versatility and use in different fields such as medicine, biology, catalysts and material science[1-8]. While 12-polyacids have been extensively studied, but studies on 6-polyacids are limited. A few well studied polyoxoanions are (i) $[W_6O_{19}]^{2-}$ (ii) $[Mo_6O_{19}]^{2-}$ (iii) $[Nb_6O_{19}]^{8-}$ and (iv) $[V_6O_{19}]^{8-}$. These polyoxometalates have weakly basic oxo-groups which render such clusters relatively unreactive towards substitution or polymerization reactions. Nevertheless, the organometallic polyoxometalates exhibit enhanced solubility, reactivity and crystal growth properties[8]. The well known compound $K_7HNb_6O_{19}\cdot 15H_2O$, is an excellent starting material for preparing organic and organometallic derivatives[9,10] polyoxoanions. Also peripherally substituted polyoxoanions are of interest due to their improved stability[11,12]. The vanadium substituted polyoxometalates have enriched oxidizing power and hence find wide variety of applications such as catalysts in oxidation reactions. Additionally, the light absorption of the vanadium incorporated polyoxometalates exhibits red shift, thus allowing photochemistry to be performed well into the area of high intensity solar light. In this context, vanadium substituted hexaniobates may be of potential application. Infrared and Raman spectroscopy are extensively used for structural elucidation in polyoxometalate chemistry[13-16]. Here, the preparation, powder X-ray analysis, IR and Raman spectral characterization of three vanadium substituted hexaniobates *viz.*, $K_7HNb_3V_3O_{19}\cdot 3H_2O$ (**I**), $K_7HNb_2V_4O_{19}\cdot 5H_2O$ (**II**) and $K_7HNbV_5O_{19}\cdot H_2O$ (**III**) have been discussed.

EXPERIMENTAL

Potassium chloride and sodium vanadate used were of AR grade, obtained from Qualigens fine chemicals, India. Niobium oxide was obtained from E-Merck, Germany and used without further purification.

Preparation of the compounds: $K_7HNb_6O_{19}\cdot 15H_2O$ was prepared according to the literature method[17].

(i) $K_7HNb_3V_3O_{19}\cdot 3H_2O$: Solution of $K_7HNb_6O_{19}\cdot 15H_2O$ (1.1 g, 20 mL of water) was added to a warm solution of $NaVO_3$ (1.8 g, 20 mL of water). The resulting mixture was acidified to pH 6, by adding 6M hydrochloric acid, boiled for 10 min and filtered. The filtrate was saturated with potassium chloride. A light violet coloured product salted out was washed with 95 % ethanol, air dried and purified by repeated recrystallization from water. Found (%): K, 24.5; Nb, 25.9; V, 13.8; $K_7HNb_3V_3O_{19}\cdot 3H_2O$ requires K, 24.8; Nb, 26.2; V, 14.3 %.

(ii) $K_7HNb_2V_4O_{19}\cdot 5H_2O$: To a solution of $NaVO_3$ (1.8 g 20 mL of water), a warm solution of $K_7HNb_6O_{19}\cdot 15H_2O$ (1.1 g 20 mL of water) was added. The mixture was acidified to pH 5.5, by adding glacial acetic acid and boiled for 2 h, filtered and cooled. To the filtrate equal volume of ethanol was added. The resulting solution was saturated with potassium chloride to salt out the product, which was further purified by recrystallization from hot water. Found (%): K, 24.4; Nb, 17.1; V, 18.9; $K_7HNb_2V_4O_{19}\cdot 5H_2O$ requires K, 24.9; Nb, 17.5; V, 19.2.

(iii) $K_7HNbV_5O_{19}\cdot H_2O$: $K_7HNb_6O_{19}\cdot 15H_2O$ solution (1.1 g 20 mL of water), was added to a warm aqueous solution of sodium vanadate (1.8 g, 20 mL water). The resultant mixture was slowly heated to 70 °C, acidified to pH 2.5 by adding 3M sulphuric acid and boiled for 2 min. Finally the solution was filtered and the filtrate was saturated with KCl to salt out the compound. Finally the compound was purified by repeated recrystallization from hot water. Found (%): K, 27.4; Nb, 10.1; V, 26.8; $K_7HNbV_5O_{19}\cdot 5H_2O$ requires K, 27.9; Nb, 9.8; V, 27.0.

Analytical and physical methods: Niobium was estimated gravimetrically as oxide according to the literature method[17]. Vanadium was estimated spectrophotometrically as a citrate complex[18]. The amount of water content was determined by heating the sample at 120 °C to constant weight. IR spectra were recorded on a Perkin Elmer 783 spectrometer as KBr disks. Raman spectra were recorded using DILOR 24 Raman spectrometer with Spectra Physics 164 Argon Laser (488 nm, 300 mw), by pressing the sample into a matrix. SEIFERT X-ray powder diffractometer was utilized to record the powder patterns of the compounds with CuK_{α_1} radiation.

RESULTS AND DISCUSSION

The powder X-ray diffraction patterns for the compounds (**I**), (**II**) and (**III**) are given in Fig. 1. Using h, k, l values of a structurally similar compound, *viz*., $[CN_3H_6]_5H[V_2W_4O_{19}]\cdot H_2O$, which possesses for the compounds (**I**), (**II**) and (**III**) were computed by a least-square programme. These values thus obtained (Table-1) show that the compounds (**I**), (**II**) and (**III**) are isomorphous. Hence one may conclude that the vanadium substitution has not altered the structure. A number of other realated ions, $[M_6O_{19}]^{8-}$ (where M = V, Nb and Ta) are also found to have similar cubic structure[19,20].

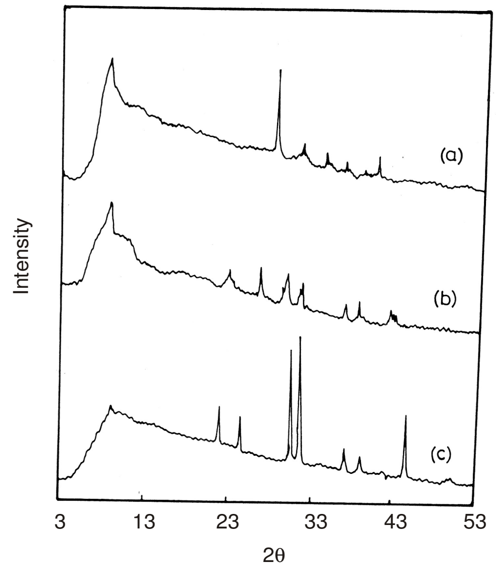

Fig. 1. X-Ray powder diffraction patterns of (a) $K_7HNb_3O_{19}\cdot 3H_2O$, (b) $K_7HNb_2V_4O_{19}\cdot 5H_2O$ and (c) $K_7HNbV_5O_{19}\cdot H_2O$

TABLE-1
LATTICE PARAMETERS FOR THE VANADIUM SUBSTITUTED HEXANIOBATES

Compounds	Cubic (Å)	Density (g cm^{-3})
$K_7H[Nb_3V_3O_{19}]\cdot 3H_2O$	13.48	4.10
$K_7H[Nb_2V_4O_{19}]\cdot 5H_2O$	13.40	3.90
$K_7H[NbV_5O_{19}]\cdot H_2O$	13.31	3.81
$[CN_3H_6]_5[V_2W_4O_{19}]\cdot H_2O$*	14.27	3.36

*From reference (11).

Vibrational spectra: The anions $[Nb_3V_3O_{19}]^{8-}$, $[Nb_2V_4O_{19}]^{8-}$ and $[NbV_5O_{19}]^{8-}$ may be considered to be formed by progressively replacing the niobium atoms by vanadium in the $[Nb_6O_{19}]^{8-}$ unit, which is found to have octahedral structure in $K_7HNbV_5O_{19}\cdot H_2O$[21]. Knowledge of the different type of metal-oxygen bonds helps the analysis of the vibrational spectra. For example, the nineteen oxygen atoms present in $[Nb_6O_{19}]^{8-}$ may be divided into the three groups, (i) six terminal oxygen atoms (O_t), attached to six niobium atoms, (ii) twelve bridging oxygen atoms (O_b), common to two octahedral and (iii) one central oxygen atom (O_c), common to six octahedra.

The IR spectra of vanadium substituted hexaniobates are given along with that of the parent compound, $K_7HNbV_5O_{19}\cdot H_2O$. The IR and Raman spectra of the complexes **I**, **II** and **III** are given in Figs. 2 and 3, respectively. The frequencies and tentative assignments are presented in Table-2. The vibrational frequencies and assignments are presented in Table-3. These assignments are based on the following discussion[21]. The total of 69 vibrational modes, expected for the octahedron $[M_6O_{19}]^{8-}$.

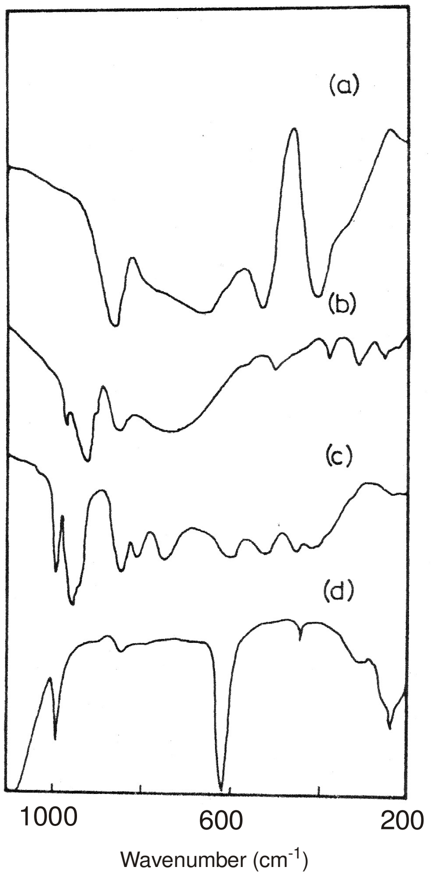

Fig. 2. IR spectra of (a) $K_7H[Nb_6O_{19}]\cdot 6H_2O$, (b) $K_7H[Nb_3V_3O_{19}]\cdot 3H_2O$, (c) $K_7H[Nb_2V_4O_{19}]\cdot 5H_2O$ and (d) $K_7H[NbV_5O_{19}]H_2O$ as KBr disks

$$\Gamma_{vib} = 3A_{1g}(R) + A_{2g} + 4E_g(R) + 3F_{1g} + 4F_{2g}(R) + A_{2u} + E_u + 7F_{1u}(i.r) + 4F_{2u}$$

Among these seven modes are infrared active and eleven are Raman active. But only six bands are observed for $[Nb_6O_{19}]^{8-}$ (Table-2). This is because different type of vibrations in the anion may have closely spaced energies and hence it

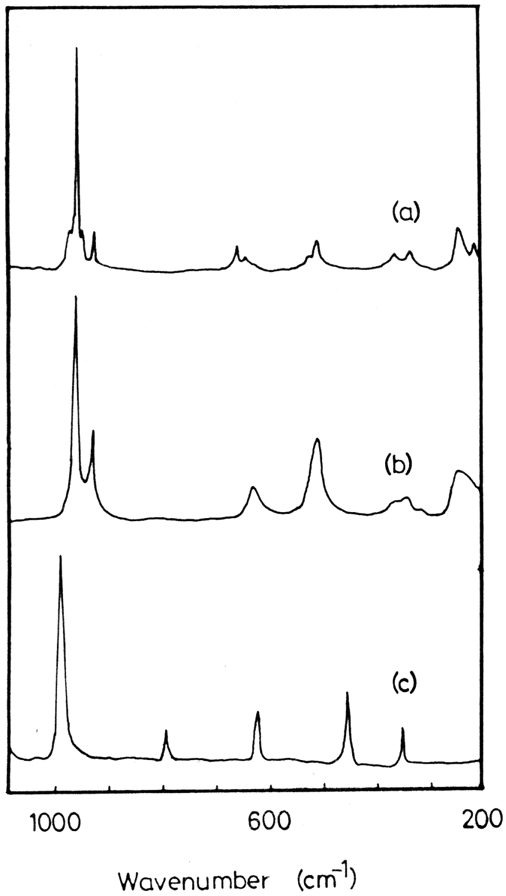

Fig. 3. Raman spectra of (a) $K_7H[Nb_3V_3O_{19}]\cdot 3H_2O$, (b) $K_7H[Nb_2V_4O_{19}]5H_2O$ and (c) $K_7H[NbV_5O_{19}]H_2O$ recorded by pressing the sample into a solid matrix

TABLE-2
IR SPECTRAL DATA* OF THE ANIONS** $[Nb_6O_{19}]^{8-}$, $[Nb_3V_3O_{19}]^{8-}$, $[Nb_2V_4O_{19}]^{8-}$ AND $[NbV_5O_{19}]^{8-}$

$[Nb_6O_{19}]^{8-}$	$[Nb_3V_3O_{19}]^{8-}$	$[Nb_2V_4O_{19}]^{8-}$	$[NbV_5O_{19}]^{8-}$	Band assignments$^{\#}$
–	960	990	990	ν_s(V-O$_t$)
–	920	950	–	ν_{as}(V-O$_t$)
860	850	850	850	ν_s(Nb-O$_t$)
–	–	810	–	ν_{as}(Nb-O)$_t$
–	750	750	620	ν_s(V-O$_b$)
–	–	600	–	ν_{as}(V-O$_b$)
670	500	530	450	ν_s(Nb-O$_b$)
530	–	450	–	ν_{as}(Nb-O$_b$)
410	390	410	320	ν(M-O$_c$)
320	320	330	290	δ(O$_b$-M-O$_t$)
225	260	260	250	δ(O$_b$-M-O$_b$) [M = V or Nb]

*cm^{-1}, KBr disks, ** Potassium is the counter cation for all the anions assignments based on the reference (21).

may not be possible to observe all the predicted vibrations[22]. Band at 860 cm^{-1} arises due to symmetric out-of-phase stretching of Nb-O$_t$ bond. Other bands at 670 and 530 cm^{-1} are assigned to the stretching of Nb-O$_b$ bonds, whereas the band at 410 cm^{-1} may correspond to Nb-O$_c$ bond.

In Raman spectrum of $[Nb_6O_{19}]^{8-}$ the high frequency A$_{1g}$ mode (890 cm^{-1}) arises due to the in-phase stretching of the peripheral Nb-O$_t$ bonds[21]. The out-of-phase stretching of Nb-O$_t$ terminal bond appears around 835 cm^{-1}. Low frequency band at 285 cm^{-1} (Raman) corresponds to the A$_{1g}$ breathing mode of metal and bridging oxygen atoms.

TABLE-3
RAMAN SPECTRAL DATA* OF THE ANIONS** $[Nb_6O_{19}]^{8-}$, $[Nb_3V_3O_{19}]^{8-}$, $[Nb_2V_4O_{19}]^{8-}$ AND $[NbV_5O_{19}]^{8-}$

$[Nb_6O_{19}]^{8-}$	$[Nb_3V_3O_{19}]^{8-}$	$[Nb_2V_4O_{19}]^{8-}$	$[NbV_5O_{19}]^{8-}$	Band assignments$^{\#}$
–	943	945	987	ν_s(V-O$_t$)
–	936	–	–	ν_{as}(V-O$_t$)
890	907	915	794	ν_s(Nb-O$_t$)
835	–	–	–	ν_{as}(Nb-O$_t$)
–	646	623	623	ν_s(V-O$_b$)
–	630	–	564	ν_{as}(V-O$_b$)
537	513	503	454	ν_s(Nb-O$_b$)
455	500	–	–	ν_{as}(Nb-O$_b$)
285	331	343	353	ν(M-O$_c$)
220	250	248	–	δ(O$_b$-M-O$_b$) [M = V or Nb]

*cm^{-1}, solid sample, **Potassium is the counter cation for all the anions assignments based on the reference (21).

In general, in the IR spectra of $[M_6O_{19}]^{8-}$ anions (where M = Nb, Ta and V), bands above 800 cm^{-1} are attributed to the stretching of peripheral M-O$_t$ bonds. Bands in the middle frequency region, 800-400 cm^{-1} are assigned to M-O$_b$ bonds. The low frequency bands (between 400-300 cm^{-1}) correspond to M-O$_c$ bond. Having given a brief analysis of the parent compound, we now proceed to analyse the substituted compounds.

High frequency region (above 800 cm^{-1}): Compounds (**I**), (**II**) and (**III**) show number of IR bands than the parent compound (**IV**). This is indicative of the low symmetry of the substituted compounds[23]. The bands appearing above 900 cm^{-1} are assigned to the V-O$_t$ stretching. This is based on the fact that the M-O$_t$ bonds have double bond character[24] and for V=O the stretching vibration occurs[25] at the spectral region 970 cm^{-1}. Vanadium substituted niobates have two types of fragments *viz.*, NbO$_6$ and VO$_6$ octahedra. Each octahedron has its own terminal, bridging and central oxygen atoms. During the replacement of niobium by vanadium in the $[Nb_6O_{19}]^{8-}$ anion, bond angles and bond distances of the vanadium substituted anions may get distorted. This is revealed in the X-ray crystal structure investigation[11] of $[(C_4H_9)]_4(NbW_5O_{18})_2O$. The vibrational interaction between the two types of fragments within the co-ordination sphere can cause the distortion, which can change the stretching frequencies of the terminal M-O$_t$ bonds. This may account for the downward shift, from 860-850 cm^{-1}, Nb-O$_t$ stretching of the substituted hexaniobates.

Middle frequency region (between 800-400 cm^{-1}): $[M_6O_{19}]^{8-}$ has close packed structure and hence the vibrations corresponding to M-O$_b$ bonds get mingled with the other modes of vibrations. This makes assignments in the middle frequency region[25] complex. Nevertheless, we have assigned the bands tentatively. The displacement of stretching frequencies of M-O$_b$ bonds as compared with that of the 'parent', $[Nb_6O_{19}]^{8-}$ in this region (both IR and Raman), suggests possible distortion in MO$_6$ octahedra upon vanadium substitution.

Low frequency region (below 400 cm^{-1}): Assignments of bands in the low frequency region are difficult because the breathing mode vibration is a mixture of bending and stretching character of M-O_t bonds[25]. The low frequency modes in the region 400-300 cm^{-1}, present both in IR and Raman spectra, are assigned to M-O_c bonds. The high intensity observed for the Raman bands in the region 300-200 cm^{-1} for compounds (**I**) and (**II**) suggests that the metal-metal interaction in the vanadium substituted hexaniobates is significant[26].

Geometry of the compounds: The possible geometry of the compounds (**I**), (**II**) and (**III**) can be arrived out by analyzing their vibrational spectra in the high frequency region, as it has been attempted earlier[21] for the Lindqvist-Aronson type anion, $[Nb_6O_{19}]^{8-}$.

(i) $[Nb_3V_3O_{19}]^{8-}$: Two different symmetries *viz.*, C_{3v} and C_{2v} are possible for this anion (Fig. 4). For C_{3v} symmetry, the expected modes of vibration for peripheral M-O_t (M = V or Nb) bonds are:

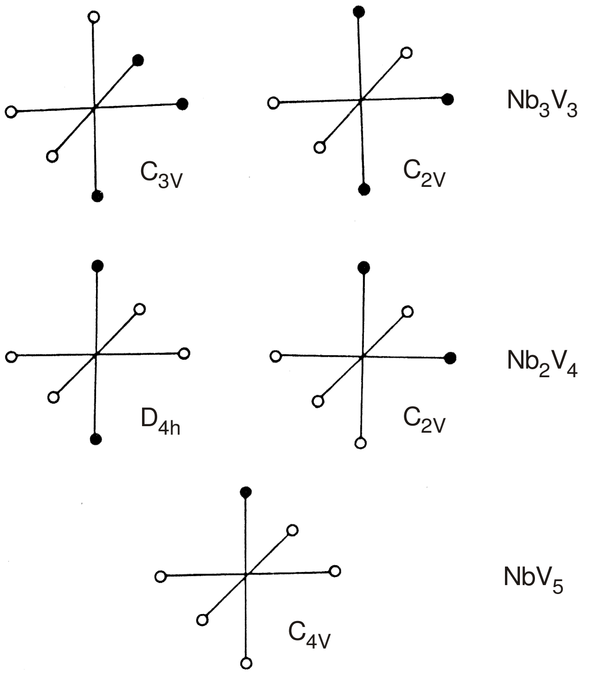

Fig. 4. Schematic representation of various configurations: black circles, niobium atoms; blank circles, vanadium atoms

$$\Gamma Nb\text{-}O_t = A_1 \text{ (i.r., R)} + E \text{ (i.r., R)}$$
$$\Gamma V\text{-}O_t = A_1 \text{ (i.r., R)} + E \text{ (i.r., R)}$$

and for C_{2v} symmetry the modes are:

$$\Gamma Nb\text{-}O_t = 2A_1 \text{ (i.r., R)} + B_1 \text{ (i.r., R)}$$
$$\Gamma V\text{-}O_t = 2A_1 \text{ (i.r., R)} + B_2 \text{ (i.r., R)}$$

Thus for C_{2v} symmetry, two bands (doublet) are expected for the Nb-O_t bonds in the high frequency region, whereas for C_{3v} symmetry only one band (A_1 type), active in both IR and Raman, is expected for the Nb-O_t stretching. Experimentally, however, only one band (A_1 type, active in both IR and Raman) is observed for the Nb-O_t in the IR spectrum, suggesting the possible symmetry for the anion, $[Nb_3V_3O_{19}]^{8-}$ to be C_{3v}. Further, the observation of a band at 500 cm^{-1} region, both Raman and IR spectra also supports (as per the mutual-exclusion principle) the non-centro symmetric structure of the anion.

(ii) $[Nb_2V_4O_{19}]^{8-}$: The two different possible configurations for these anions are given in Fig. 5. Vibrational modes of terminal bonds M-O_t (M = V or Nb) can be worked out to be:

$$\Gamma Nb\text{-}O_t = A_1 \text{ (i.r., R)} + B_1 \text{ (i.r., R)}$$
$$\Gamma V\text{-}O_t = 2A_1 \text{ (i.r., R)} + B_1 \text{ (i.r., R)} + B_2 \text{ (i.r., R)}$$

for C_{2v} symmetry and

$$\Gamma Nb\text{-}O_t = A_1 \text{ (i.r., R)}$$
$$\Gamma V\text{-}O_t = 2A_1 \text{ (i.r., R)} + B_1 \text{ (R)} + E \text{ (i.r., R)}$$

for D_{4h} symmetry. Thus for C_{2v} symmetry two bands one symmetric and one asymmetric (active in both IR and Raman) are expected at the high frequency region. On the contrary for D_{4h} symmetry only one band is expected. However, there are two bands at 810 and 850 cm^{-1} and these bands are assigned to symmetric and asymmetric stretching vibrations of Nb-O_t bonds (Table-2), thus indicating C_{2v} symmetry for $[Nb_2V_4O_{19}]^{8-}$.

(iii) $[NbV_5O_{19}]^{8-}$: For this anion, the only possible symmetry is C_{4v} (Fig. 5). The expected vibrational modes for the anion are,

$$\Gamma_{vib} = 14A_1 \text{ (i.r., R)} + 4A_2 + 9B_1 \text{ (R)} + 6B_2 \text{ (R)} + 18E \text{ (i.r., R)}$$

Various bands observed are listed in Tables 1and 2. A unique feature of the IR spectrum of this anion is the high intensity of the band at 620 cm^{-1}. This may be accounted as follows. The O_b-M-O_t bond angle is maximum for the less substituted $[M_6O_{19}]^{8-}$ anion[25]. When more number of niobium atoms are replaced by vanadium atoms, the bond angle between bridging and terminal oxygen atoms get reduced. As a result, the M-O_b stretching's may have closely spaced phonon energies, which may result in a strong band at 620 cm^{-1} for the anion (**III**).

Conclusion

Three well-defined vanadium substituted hexaniobates have been synthesized. The geometry of the compounds $K_7HNb_3V_3O_{19}\cdot 3H_2O$ (**I**) $K_7HNb_2V_4O_{19}\cdot 5H_2O$ (**II**) $K_7HNbV_5O_{19}\cdot H_2O$ (III) have been arrived by IR and Raman spectroscopy. It would be further interesting to study the redox properties of these compounds. However, the efforts in this direction were hampered by the very poor solubility of these compounds.

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