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Cation-Dependent Self-assembly of Vanadium Polyoxoniobates

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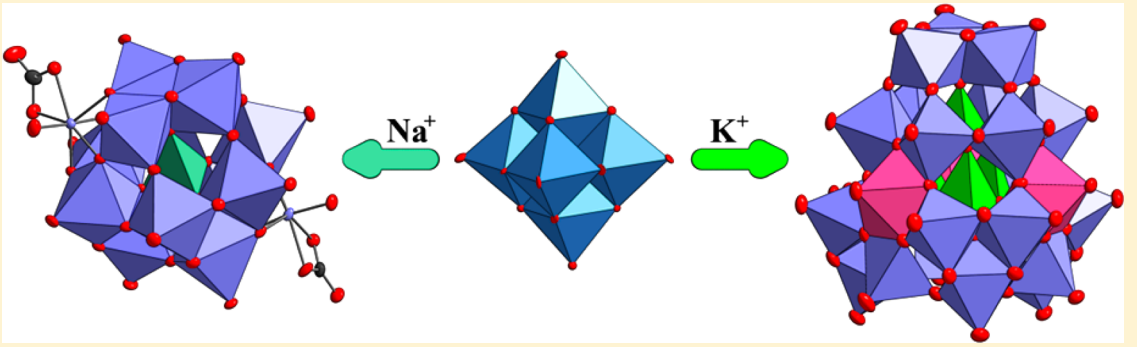
Supporting Information



ABSTRACT: Reaction of $Na_7H[Nb_6O_{19}]\cdot 15H_2O$ with $NaVO_3\cdot 2H_2O$ at 220 °C in the presence of $NaHCO_3$ gives new bicapped α-Keggin vanadododecaniobate $[VNb_{12}O_{40}\{NbO(CO_3)\}_2]^{13-}$, isolated and structurally characterized as $Na_9H_4[VNb_{12}O_{40}\{NbO(CO_3)\}_2]\cdot 37H_2O$ (**1**). According to ^{51}V NMR and ESI-MS data, this anion equilibrates in solution with $[VNb_{12}O_{40}]^{15-}$ and oligomeric species that result from dissociation of the $\{NbO(CO_3)\}^+$ fragments. In the presence of potassium, the same reaction gives $[V_xNb_{24}O_{76}]^{n-}$ (x = 4, n = 12 (**2a**); x = 3, n = 17 (**2b**)). The anions with x = 3 and 4 cocrystallize together, but exist as separate entities both in solid and in solution according to ^{51}V MASS NMR and ESI-MS data.

INTRODUCTION

The chemistry of niobium polyoxocomplexes (polyoxoniobates, PONb) is a challenging area of polyoxometalate chemistry, experiencing a spectacular renaissance.[1] Besides unique solution behavior defined by extraordinary strong cation association, the PONb show photocatalytic activity in water splitting,[2] which constitutes a hot topic in modern chemistry.[3] One of the problems in the chemistry of PONb is finding conditions for producing of larger, nanosized polyoxocomplexes—nanosized models of Nb_2O_5. The most common way to achieve this is thermal induction of the PONb aggregation from hexaniobates $[Nb_6O_{19}]^{8-}$ at different pHs. In this way, transient $\{Nb_7O_{22}\}^{9-}$ building blocks are generated, which combine into trimeric $[Nb_{24}O_{72}]^{14-}$ or larger aggregates.[4] Cronin et al. studied this aggregation in solutions of $K_7H[Nb_6O_{19}]\cdot 13H_2O$ at 200 °C and were able to detect the formation of larger $\{Nb_{10}\}$, $\{Nb_{20}\}$, and $\{Nb_{27}\}$ isopolyniobates, and isolate $[HNb_{27}O_{76}]^{16-}$ and $[H_{10}Nb_{31}O_{93}(CO_3)]^{23-}$.[5] Both complexes contain a rare pentagonal $\{(Nb)Nb_5\}$ building block, which had been observed only in Nb oxides.[6] The existence of such a unit indicates a link to the chemistry of giant polymolybdates, where the pentagonal $\{(Mo)Mo_5\}$ building blocks steer aggregation toward spherical and wheel-shaped nanoscale POMs like Mo blues or keplerates.[7] In the structure of $[HNb_{27}O_{76}]^{16-}$, there are four tetrahedral cavities inside the backbone, and a large crown-ether like cavity in the bottom part. This means that heteroatoms with stable tetrahedral arrangements (V^V, P^V, As^V) could stabilize such structures. Vanadium and phosphorus are the most suitable to prove this suggestion experimentally, both from their smaller size and amenability to NMR studies. In this contribution, we report hydrothermal rearrangements of sodium and potassium hexaniobates in the presence of $NaVO_3$ as vanadium source, leading to vanadoniobates of two distinct types.

EXPERIMENTAL SECTION

General Information. Starting hexaniobates $A_7H[Nb_6O_{19}]\cdot nH_2O$ (A = Na, n = 15; A = K, n = 13) were prepared according to the published procedures.[8] TG experiments were done on a NETZSCH TG 209 F1 device in an Al_2O_3 crucible by heating a sample from 22 to 300 °C with a 10 °C gradient. IR spectra (4000–400 cm^{-1}) were recorded on a Vertex 80 spectrometer. Raman spectra (60–4000 cm^{-1}) were obtained on a Triplemate spectrometer (Spex, USA) equipped with a multichannel detector LN-1340 PB (Princeton Instruments, USA). EDX analysis was performed on a HITACHI TM 3000 Tabletop Microscope. Elemental analysis for **1** and **2** was carried out on a high-resolution spectrometer iCAP-6500 (Thermo Scientific) with a cyclone type spray chamber and "SeaSpray" nebulizer. NMR

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spectra were run on a Bruker Avance III 500 spectrometer at room temperature with addition of a very small amount of D_2O to the sample aqueous solutions. The ^{51}V chemical shift was referenced to external $VOCl_3$ (δ = 0 ppm) as standard. The total sweep covered from −1000 to 0 ppm. Solid state NMR experiments were run on a Bruker Avance III 500 spectrometer at 5−15 kHz.

Synthesis of $Na_9H_4[VNb_{12}O_{40}\{NbO(CO_3)\}_2]\cdot 37H_2O$ (1). Solid $Na_7H[Nb_6O_{19}]\cdot 15H_2O$ (0.400 g, 0.31 mmol), $NaVO_3\cdot 2H_2O$ (0.046 g, 0.31 mmol), and $NaHCO_3$ (0.150 g, 1.79 mmol) were dissolved in 10 mL of distilled water upon heating and stirring (pH 13.0). The solution was transferred into a stainless steel autoclave (the volume of the Teflon cartridge was 30 mL), and the mixture was kept at 220 °C for 18 h. After cooling, a colorless precipitate was filtered off (final pH was 10.3), and the filtrate was reduced in volume by heating at 90 °C to 3 mL. The concentrated solution was placed into a vial for slow evaporation. Rhombohedral colorless crystals were collected by filtration, rinsed with deionized water, and dried in air. Recrystallization from deionized water gave colorless crystals of **1**. Yield 0.131 g (13%) based on niobium. EDX: atomic ratio Na:Nb:V - 9.1:13.8:1.0. ICP-AES found Na, Nb, V (%): 6.7, 43.6, 1.5, calculated for **1**: Na, Nb, V (%): 6.9, 43.8, 1.7. ^{51}V NMR (H_2O + D_2O, r.t., δ, ppm): −481.3; −487.1; −492.8; −532.1. ^{51}V MASS NMR: −530 ppm. ^{13}C MASS NMR: −166 ppm. IR (KBr, ν, cm^{-1}): 3418 (s), 1604 (m), 1459 (m), 1340 (m), 1053 (w), 874 (s), 800 (s), 656 (s), 581 (s), 461 (s), 401 (s). Raman (ν, cm^{-1}): 1065 (m), 913(vs), 856(s), 368 (m), 250(m), 215 (m). TGA: weight loss 13% corresponds to the removal of 30 water molecules.

Synthesis of 2, Containing Potassium Salts of $[Nb_{24}O_{76}V_4]^{12-}$ (2a) and $[V_3Nb_{24}O_{76}]^{17-}$ (2b). Solid $K_7H[Nb_6O_{19}]\cdot 13H_2O$ (0.400 g, 0.30 mmol), $NaVO_3\cdot 2H_2O$ (0.046 g, 0.31 mmol), and $NaHCO_3$ (0.150 g, 1.79 mmol) were dissolved in 10 mL of water upon heating and stirring (pH 13.0). The final solution was transferred into a stainless steel autoclave (30 mL Teflon cartridge), and the mixture was kept at 220 °C for 18 h. After cooling, a colorless precipitate was filtered off (final pH was 10.3), and the filtrate was reduced by heating at 90 °C to 3 mL volume. This concentrated solution was placed into a vial and left for crystallization. Overnight, hexagonal plate colorless crystals appeared and were collected by filtration, rinsed with deionized water, and dried in air. Repeated recrystallizations from small amounts of deionized water produced hexagonal plates suitable for X-ray analysis. Yield of **2** 0.07 g (4%) based on niobium. ^{51}V NMR (H_2O + D_2O, r.t., δ, ppm): −532.5. ^{51}V MASS NMR: −532 (m). Raman (ν, cm^{-1}): 1065 (m), 935(vs), 919(s), 907(s), 867 (m), 647 (m), 498 (m), 360 (m), 329 (m), 244 (m), 211 (m). TGA: weight loss 16% that corresponds to removal of 42 water molecules. EDX: atomic ratio K:Na:Nb:V is 1.6:2.3:6.7:1. ICP-AES: found K, Na, Nb, V (%): 4.4, 4.3, 46.2, 3.5, calculated for $K_6Na_{8.5}[Nb_{24}V_{3.5}O_{76}]\cdot 42H_2O$ (as 0.5/0.5 mixture of **2a** and **2b**) K, Na, Nb, V (%): 4.9, 4.1, 46.4, 3.7.

Electrospray Ionization Mass Spectrometry (ESI-MS). The experiments were performed on a hybrid linear ion trap FTICR mass spectrometer LTQ-FT (Thermo Fisher Scientific, Bremen, Germany) equipped with a 7 T supra-conducting magnet by infusion. The mass spectrometer was first tuned and calibrated in the negative mode following the standard optimization procedure for all voltages and settings. The complex was dissolved in 80% H_2O, and 20% methanol was added for ionization. The transfer capillary temperature was set at 175 °C. Mass spectra were recorded in full scan from 200 to 2000 Da with a resolution of 100.000 at m/z 400. The data were processed with the Xcalibur software version 2.1.

X-ray Diffraction. The diffraction data were collected at 150 K on a Bruker Apex Duo (for **1**) and on an Xcalibur (Agilent Technologies) at 130 K (for **2**) single crystal diffractometers with Mo Kα radiation (λ = 0.71073 Å) by doing ω and φ scans of narrow (0.5°) frames. The structures were solved by direct methods and refined with full-matrix least-squares treatment against $|F|^2$ in anisotropic approximation with SHELX 2014/7[9] in the ShelXle program.[10] Absorption corrections were applied empirically with SADABS[11] and SCALE3 ABSPACK programs (CrysAlisPro 1.171.38.41 (Rigaku OD, 2015)). Crystallographic data and refinement details for **1** and **2**are listed in Table S1, and main bond distances for **1** are listed in Table S2.

Crystals of **2** grow as aggregates of thin poorly diffracting hexagonal plates, and the XRD data collection was done from a twinned crystal that gave a mediocre R value. Composition of **2** was assigned with the help of EDX, TGA, and ESI-MS data.

Crystallographic data files for **1** and **2** have been deposited with ICSD (Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany; e-mail: crysdata@fiz-karlsruhe.de) with numbers CSD 431897 (**1**), CSD 431896 (**2**).

RESULTS AND DISCUSSION

Synthesis and Structure of 1. Heating a mixture of sodium metavanadate and sodium hexaniobate at 220 °C (initial pH 12) for 18 h produces a copious amorphous material and a clear colorless solution, which contains two distinct types of vanadates, according to ^{51}V NMR data—mainly the cyclic tetravanadate $[V_4O_{12}]^{4-}$ (which is the dominant form of vanadate at C_v 10^{-2} M and pH 8−10;[12] the final pH dropped to 10.3), together with a small amount of a new product. The controlled evaporation solution gave a tiny amount of hexagonal plates of $Na_9H_4[VNb_{12}O_{40}\{NbO(CO_3)\}_2]\cdot 37H_2O$ (**1**). The incorporation of carbonate was due to absorption of CO_2 from air by the strongly basic solution of hexaniobate. Consequently, addition of $NaHCO_3$ significantly improves the yield of **1** (up to 13%) and makes it possible to study its chemistry.

The vanadatotetrakaidekaniobate $[VNb_{14}O_{42}(CO_3)_2]^{13-}$ anion present in **1** (Figure 1) has an α-Keggin-type structure

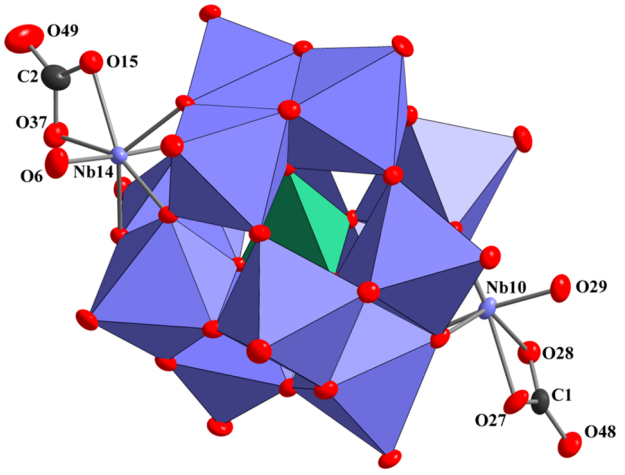

Figure 1. Structure of $[VNb_{14}O_{42}(CO_3)_2]^{13-}$ (thermal ellipsoids drawn with 50% probability). Main bond distances: d(O6−Nb14) = 1.772(7) Å; d(O15−Nb14) = 2.181(7) Å; d(O37−Nb14) = 2.149(7) Å; d(O27−Nb10) = 2.175(7) Å; d(O28−Nb10) = 2.170(6) Å; d(O29−Nb10) = 1.774(7) Å; $d(V-O)_{av}$ = 1.695(6) Å.

with two extra $\{NbO(CO_3)\}^+$ caps, where the niobium atom has coordination number 7. BVS for oxygen atoms of CO_3^{2-} (Table S3) agrees with partial protonation of O49. This mode of capping is typical for highly charged heterododecaniobates: in $K_{12}(Ti_2O_2)[SiNb_{12}O_{40}]\cdot 16H_2O$, the Keggin anions $[SiNb_{12}O_{40}]^{16-}$ are capped by additional $\{TiO\}^{2+}$ groups which unite them into infinite chains.[13] In $Na_{10}(Nb_2O_2)[TNb_{12}O_{40}]\cdot xH_2O$ (T = Si, Ge), there are additional $\{NbO\}^{3+}$ caps with a similar function.[14] However, there are also uncapped dodecaniobates, as is the case of $Na_{16}[TNb_{12}O_{40}]\cdot 4H_2O$ (T = Si, Ge).[15] Single capped germano- and silicododecaniobates, namely, $Rb_{13}[GeNb_{13}O_{41}]\cdot 23H_2O$, $Cs_{10.6}[H_{2.4}GeNb_{13}O_{41}]\cdot 27H_2O$, and $Cs_{18}H_6[(NbOH)SiNb_{12}O_{40}]_2\cdot 38H_2O$, were isolated.[16] Small

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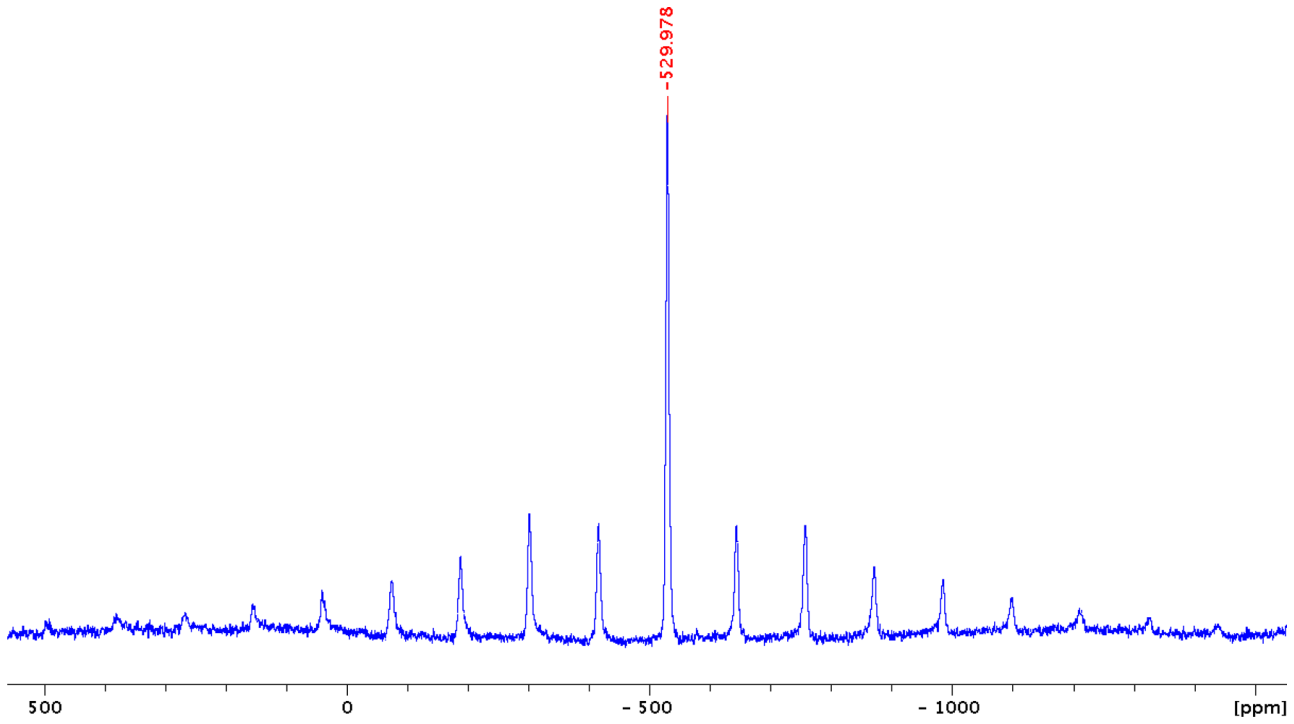

Figure 2. ^{51}V MASS NMR spectrum of **1**.

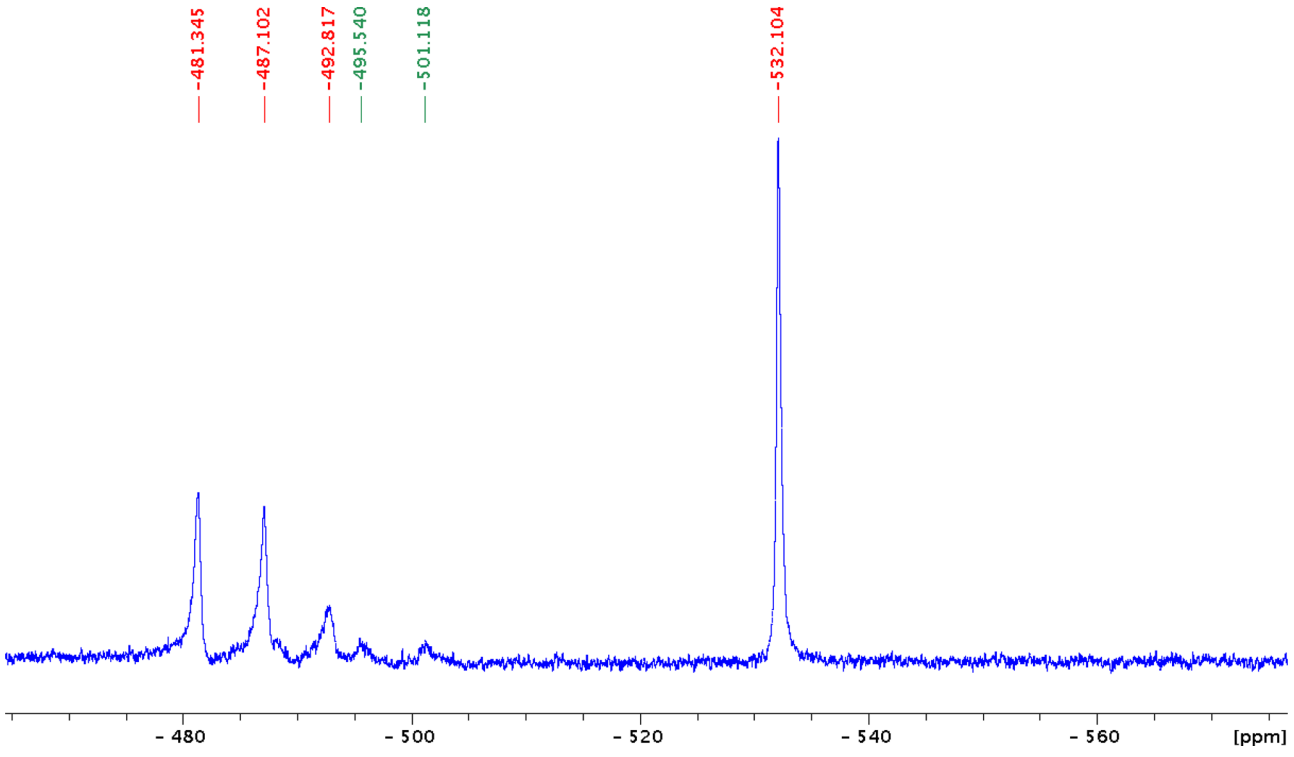

Figure 3. ^{51}V NMR spectrum of the solution of **1** at natural pH.

angle X-ray scattering (SAXS) studies on the solutions of $Rb_{13}[GeNb_{13}O_{41}]\cdot 23H_2O$ and $Cs_{10.6}[H_{2.4}GeNb_{13}O_{41}]\cdot 27H_2O$ revealed oligomerization of the monomers into the chain structures through the dimerization of the $\{NbO\}^{3+}$ caps. The extent of the oligomerization is controlled by pH, concentration, and the counterion, and chains built of up to six Keggin links with large were observed in the presence of large alkali metal cations. In our case, the polymerization of the $[VNb_{12}O_{40}\{NbO\}_2]^{10-}$ bicapped Keggin anions is blocked by coordination of CO_3^{2-} to the coordinatively unsaturated capping Nb atoms (CN would be 5 without carbonate). The main bond distances in $[VNb_{14}O_{42}(CO_3)_2]^{13-}$ are listed in Figure 1.

The lighter analogue of niobium—vanadium—also forms a similar bicapped Keggin anion $[PV_{14}O_{42}]^{9-}$, but under strongly *acidic* conditions.[17] Due to the smaller ionic radius of V^{5+}, it

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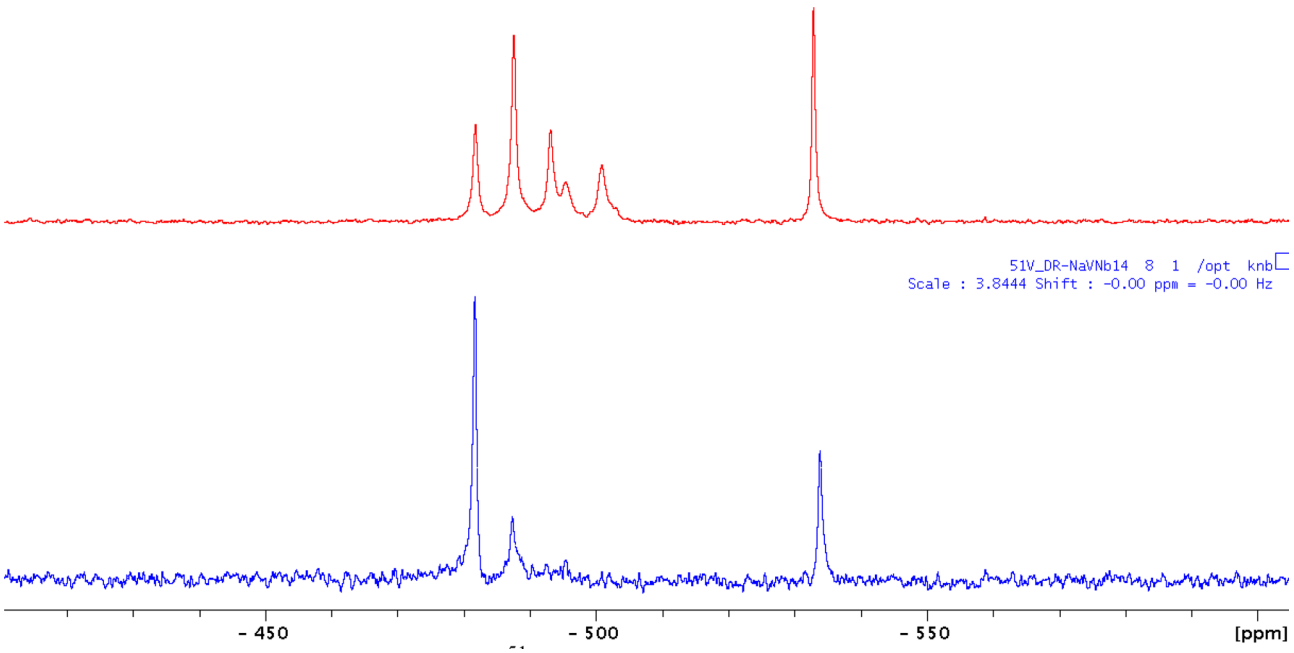

Figure 4. Concentration dependence of ^{51}V NMR signals in **1**. Upper spectrum recorded for 4.7 mM, lower for 0.8 mM aqueous solutions.

shows no tendency to polymerize into the chains and apparently exists only in the monomeric form. The $\{VO\}^{n+}$ groups can also cap highly charged reduced dodecamolybdate Keggin anions, as in $[PMo_{12}O_{40}(VO)_2]^{n-}$[18] or $[GeMo_{12}O_{40}(VO)_2]^{3-}$.[19] The $[PMo_{12}O_{40}(VO)_2]^{n-}$ has been assessed as an important model for spin qubit because the redox-active core unit of the Keggin phosphomolybdate is capped on the opposed positions by two vanadyl ions (2+), each containing a localized spin of 1/2. These spins can be coupled through the electrons of the central core by electrical manipulation of the molecular redox potential owing to the change of charge.[20] The $\{VO\}^{3+}$ caps can be coordinated to Keggin-type dodecaniobates in $(TMA)_9[V_3Nb_{12}O_{42}]\cdot 18H_2O$[21] and $[Cu(en)_2]_{3.5}[Cu(en)_2(H_2O)]\{[VNb_{12}O_{40}(VO)_2][Cu(en)_2]\}\cdot 17H_2O$.[22] In this way, they can even occupy up to six vertex positions, as in $[Cu(en)_2]_4[PNb_{12}O_{40}(VO)_6](OH)_5\cdot 8H_2O$ and in $[Cu(enMe)_2]_4[PNb_{12}O_{40}(VO)_6](OH)_5\cdot 6H_2O$ (en = 1,2-ethylenediamine and enMe = 1,2-diaminopropane).[23] In our case, we used a Nb:V = 6:1 atomic ratio and no vanadyl caps entered the structure. Reactions with larger vanadium-to-niobium molar ratios are under investigation.

Recently Su et al. reported preparations of $[Na(H_2en)_5][VNb_{14}O_{42}(NO_3)_2]\cdot 12H_2O$ and $K_7Na_4[VNb_{14}O_{42}(NO_3)_2]\cdot 31H_2O$ by heating together V_2O_5, NaOH, $K_7H[Nb_6O_{19}]\cdot 13H_2O$, $Co(NO_3)_2\cdot 6H_2O$, and ethylenediamine.[24] We also tried to switch from carbonate to nitrate, but no $[VNb_{14}O_{42}(NO_3)_2]^{11-}$ was detected. It means that, under conditions as used for preparation of **1**, weakly coordinating nitrate cannot stabilize the vanadododecaniobate structure.

Solid State and Solution Studies of 1. A crystalline sample of **1** was studied with ^{51}V and ^{13}C MASS NMR techniques (Figure 2). In the ^{51}V spectrum, at a rotation speed of 15 kHz, a single line at −530 ppm from the $\{VO_4\}^{3-}$ moiety inside the bicapped Keggin was observed.

In ^{13}C MASS NMR, we found one unsymmetrical signal at 166 ppm (15 kHz) resulting from nonequal orientations of the CO_3^{2-} ligands in the crystal structure (Figure S1). These data confirm the individuality of the crystalline sample of **1**. However, dissolving **1** in water produces several species, according to ^{51}V NMR data (Figure 3). The main solution signal at −532 ppm corresponds to −530 ppm assigned to the signal from the bicapped Keggin anion in solid state.

In order to identify the other signals, we probed the solutions of $[VNb_{14}O_{42}(CO_3)_2]^{13-}$ with the ESI-MS technique (see Figure S1 and Table S4). We observed two series of signals, one from uncapped Keggin anions ($[VNb_{12}O_{40} + nNa^+ + mH^+]^{2-}$) and the other from bicapped Keggins ($[VNb_{12}O_{40}\{NbO(CH_3O)_2\}_2 + xNa^+ + yH^+]^{2-}$), respectively. The substitution of a carbonate ligand with two methoxo ligands is due to the fact that the ESI-MS spectra were recorded essentially in methanol with a small amount of water added. Consequently, we have assigned the signals in the area between −480 and −510 ppm to these species. Taking into account the reported SAXS data on the solution behavior of $[GeNb_{13}O_{41}]^{13-}$, we have also to admit that some of these signals might correspond to oligomerization of the Keggin anions through $\{Nb_2O_2\}$ bridges after the loss of carbonate.[16]

This oligomerization could not be detected under ESI-MS conditions since the concentration of the sample was below 10^{-5} M, which was much lower than that used for recording ^{51}V NMR. In order to get a more consistent picture, we have studied aqueous solutions of **1** with ^{51}V NMR by varying the concentration, and indeed found that several of these additional signals decrease at lower concentrations (Figure 4). This is consistent with the dissociation of oligomeric species. At the same time, the relative intensity of the signal at −482 ppm significantly increases with dilution, while that of the parent $[VNb_{14}O_{42}(CO_3)_2]^{13-}$ anion at −532 ppm simultaneously decreases. This can be explained by reversible dissociation of the $\{NbO\}^{3+}$ caps being favored in diluted solutions.

This experiment fixes the signal from the noncapped Keggin form $[VNb_{12}O_{40}]^{15-}$ to −482 ppm. Moreover, as a single-capped link between $[VNb_{12}O_{40}]^{15-}$ and $[VNb_{14}O_{42}(CO_3)_2]^{13-}$, we have to admit the existence of a dimer $\{[Nb_2O_2][VNb_{12}O_{40}]_2\}$.[24] If this is correct, the signal at −487 ppm can be assigned to this species.

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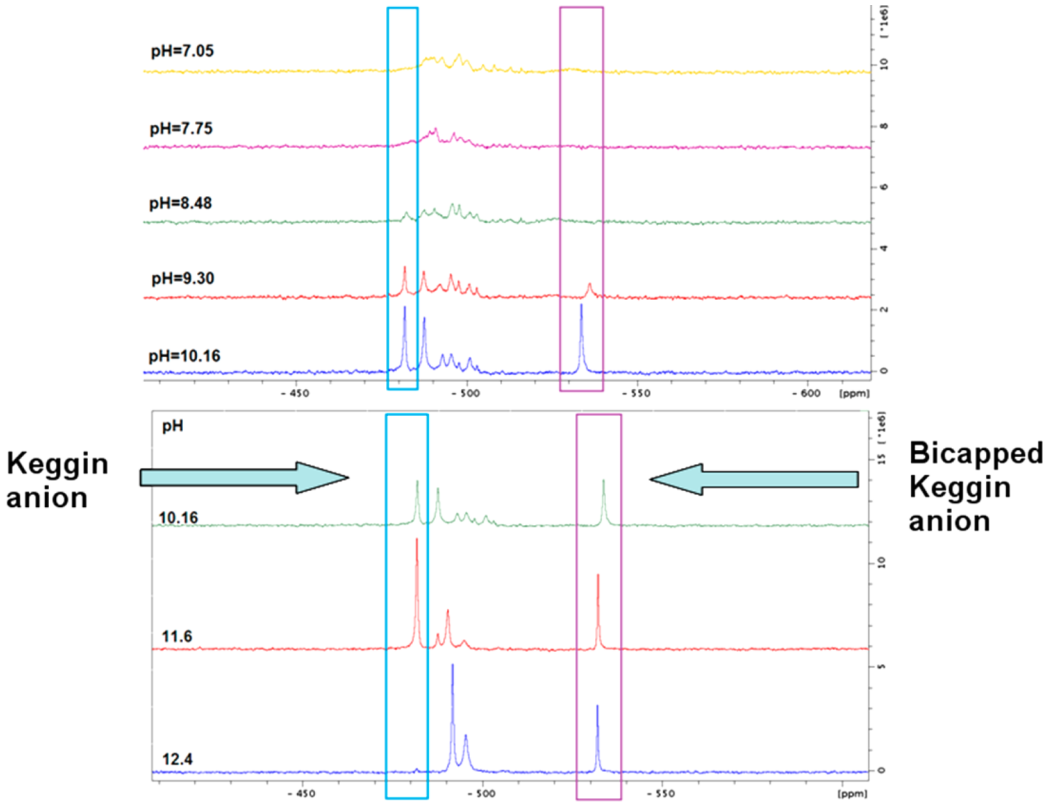

Figure 5. Dependence of ^{51}V NMR signals of **1** from pH value.

We have run ^{51}V NMR experiments at various pHs and found that the relative stabilities of the capped and noncapped Keggin ions are pH-dependent (Figure 5).

From these data, we can estimate the pH stability windows for $[VNb_{12}O_{40}]^{15-}$ and $[VNb_{14}O_{42}(CO_3)_2]^{13-}$ as being 11.6 ÷ 8.4 and 13 ÷ 9.2 pH units, respectively. At pH ≥ 12.4, $[VNb_{12}O_{40}]^{15-}$ is not detected, but the intensities of the −492 and −496 ppm peaks increase. This can be attributed to the formation of the single-capped Keggin anion $[VNb_{12}O_{40}(NbO(CO_3))]^{14-}$. Moreover, gradually reducing the pH value to 7 gives rise to an additional number of peaks clustering between −480 and −510 ppm, in accordance with the formation of (Nb_2O_2)-bridged oligomers. Finally, at pH 7, we observe only these oligomeric forms. Remarkably, no free vanadate species were detected in all of these experiments, indicating the preservation of the Keggin structure within the investigated pH window.

We could not find reference ^{51}V NMR data for "*trans*-vanadium" bicapped Keggin-type complexes $\{VNb_{12}O_{40}(VO)_2\}$,[22] nor are ^{51}V MASS NMR data available for $[Na(H_2en)_5][VNb_{14}O_{42}(NO_3)_2]\cdot 12H_2O$ and $K_7Na_4[VNb_{14}O_{42}(NO_3)_2]\cdot 31H_2O$.[24] However, ^{51}V NMR spectra of $(TMA)_9[V_3Nb_{12}O_{42}]\cdot 18H_2O$ exhibited a sharp peak at −520.0 ppm and a broad peak at −528.1 ppm with an approximate integrated intensity ratio of 1:2, corresponding to a central VO_4 and two capping {VO} units in the cluster.[21] Given the quadrupolar nature of ^{51}V, a reasonable hypothesis would be to assign the sharp signal to the symmetric VO_4, and the broader peak at −528.1 ppm to the less-symmetric capping VO_5 sites. This assignment agrees well with the ^{51}V NMR studies of the isostructural bicapped Keggin isopolyoxovanadate, $[VV_{12}O_{40}(VO)_2]^{9-}$, for which the signal from the central VO_4 was observed at −507 ppm, and VO_5 appeared at −531 ppm.[25] Furthermore, for $[PV_{12}O_{40}(VO)_2]^{9-}$, the −523 ppm peak was assigned to the VO_5 caps, and the −575 ppm peak to the VO_6 addenda.[17]

Isolation and Structure of 2. The chemistry of polyoxoniobates and tantalates is strongly influenced by the counterions. Aggregation of Lindqvist-type hexametalates with cations both in solid state and in solution is well documented.[1a] Applying these considerations to higher-nuclearity PONb, we have compared the products formed by heating hexaniobate with vanadate: (i) in the presence of sodium solely and (ii) in the presence of potassium *and* sodium. The pure Na^+ salts yielded **1**, while, in the presence of K^+, after carefully monitored evaporation of the filtrate from the reaction mixture, we obtained crystals containing $[K@V_xNb_{24}O_{76}]^{n-}$ (**2**) displaying a hitherto unprecedented anion structure (Figure 6).

The anion is built of three edge-sharing $\{NbO_6\}$ octahedra having common vertices with three fused $\{(NbO_2)(NbO_6)_5\}$ pentagonal units, which, in turn, are additionally bridged with three *trans*-$\{NbO_2\}$ fragments, all forming the polyoxoniobate backbone. Alternatively, the structure can be regarded as a hybrid of a trilacunary $\{VNb_9\}$ Keggin anion and a polyniobate based on corner-shared pentagonal $\{NbNb_5\}$ units, as found, e.g., in the hexatriakontamolybdate $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$.[7] This particular combination is apparently without precedents in the chemistry of polyoxomolybdates. There are five cavities inside the anion: four pseudotetrahedral T-cavities (with four short (1.829−2.088 Å) and two long (2.395−2.434 Å) V−O distances) inside, and a large crown-ether like lacuna at the bottom part. The T-cavities are occupied with vanadium with either full or $^3/_4$ occupancy, and the large lacuna accommodates a single K^+ cation (Figure S2). These four T-cavities form a supertetrahedral cavity with the topology of the P_4O_{10} cage.

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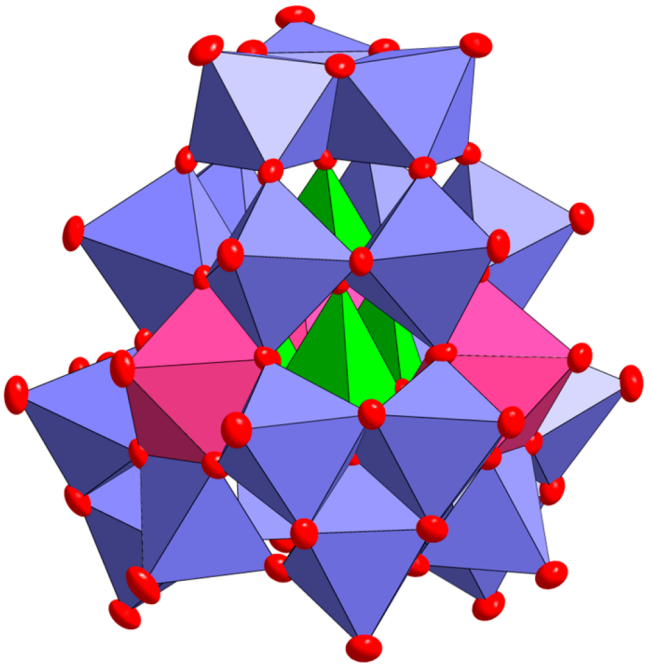

Figure 6. View of $[V_xNb_{24}O_{76}]^{n-}$ (combined ellipsoid (50% probability) and polyhedral model). Vanadium polyhedra are shown in green, niobium polyhedra with CN 7 in pink.

Due to the presence of two closely related types of anions of the same geometry in **2**, which contains cocrystallized $[V_xNb_{24}O_{76}]^{n-}$ (with $x = 4$, $n = 12$ (**2a**) and $x = 3$, $n = 17$ (**2b**)), one of the T-cavities is free (or, more probably, is occupied by a proton). The heptaeicosaniobate $K_{13}Na_3[HNb_{27}O_{76}]\cdot 25H_2O$ reported by Cronin et al. has a related structure, with one T-cavity occupied with a proton.[5] In its crystal structure, however, the PONb anions are severely disordered, which has made it difficult to refine the structure and composition of this POM. From the obvious relationship between the structures of $[V_4Nb_{24}O_{76}]^{12-}$ and $[HNb_{27}O_{76}]^{16-}$, we suggest that both anions should have the same set of T-cavities, which could be occupied with vanadium (in **2**) or niobium (in $[HNb_{27}O_{76}]^{16-}$). The only problem is that, for Nb^{5+}, this would be a very rare case of tetrahedral coordination with four O^{2-} ligands. We have compared the coordination of V^{5+} and supposed Nb^{5+} inside the T-cavities (Figure 7). In both cases, there are four short and two long M−O distances, and in the case of Nb, the coordination can be described as a highly distorted tetrahedron with two additionally coordinated oxides. Such an arrangement was found only in the rare-earth orthoniobates $LnNbO_4$ (Fergusonite-type mineral), which can also be synthesized at the temperature range between 500 and 1100 °C.[26] Accordingly to the neutron diffraction experiments, the Nb−O distances in such a tetrahedron are 1.834 Å.[27] Recently, Kolis et al. also reported about the synthesis of rare earth orthoniobates $RENbO_4$ (RE = Y, La−Lu).[28]

These compounds were grown as large single crystals in 30 M KOH at 700 °C and 2 kbar. Niobium occupies a 4e Wyckoff position having 2-fold symmetry and forms shorter bonds to four oxygen atoms with a narrow spread of distances (average Nb−O distances of 1.846(5) and 1.927(5) Å across the $RENbO_4$ family) and much longer bonds to two other oxygen atoms (average Nb−O distance of 2.455(5) Å) to form the distorted NbO_6 unit. It seems not very likely that already at 200 °C niobium would spontaneously enter such energetically disfavored positions. A kind of a structural artifact arising from the disorder is not to be discarded, and perhaps the Nb occupancies of the T-cavities in $[HNb_{27}O_{76}]^{16-}$ should, in fact, be less than 1, if not zero. Unfortunately, we also have encountered severe problems with crystal diffraction in **2** due to the formation of stacks of poorly diffracting very thin plates.

It is also interesting that, in the presence of roughly equimolar amounts of K^+ (2.17 mmol) and Na^+ (1.90 mmol) used in the preparation of **2**, it is exclusively potassium that enters the lacuna. If one compares the cation-accommodating lacuna in **2** with what is found in other polyniobates, one can cite $[K@Nb_{24}O_{72}H_9]^{14-}$, which has a very similar crown-ether like cavity flanked by six $\{NbO_6\}$ fragments. Moreover, such a cyclic structure occurs in a pyrochlore mineral $(Na,Ca)_2Nb_2O_6(OH,F)$.[29] Hence, we can suggest that this cyclic arrangement $\{K@(NbO_6)_6\}$ is energetically preferred at higher temperatures and can be generated and used as a building block for construction of various polyniobates.

Looking across the periodic table for structural analogues of **2**, we have found structures of $[H_2Ti_{28}O_{38}(OEt)_{40}LnCl]$ (Ln = La, Ce) with a closely related metal core, which also contain three pentagonal $\{(Ti)Ti_5\}$ building blocks, and has a large cavity flanked with six $\{TiO_6\}$ octahedra, occupied with a Ln^{3+} cation.[30] It is yet another example of the diagonal relationship between niobium and titanium.

Solid State and Solution Studies of 2. The solubility of **2** in water is practically the same as of KVO_3, which makes

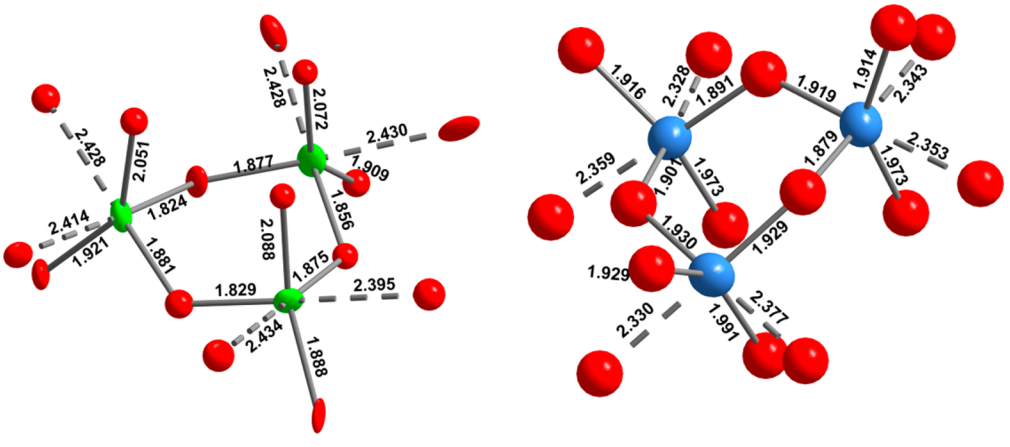

Figure 7. Comparison of the T-cavities geometry in **2** (left) and in CSD 420848 (right).

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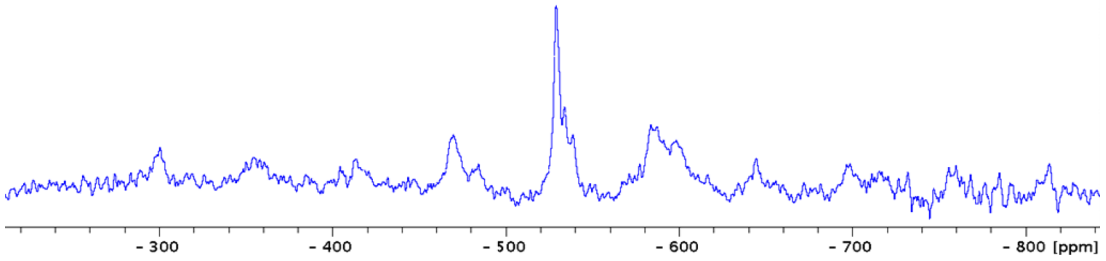

Figure 8. ^{51}V MASS NMR for **2**. Intensity of satellites is low due to low content of **2** (mixed with SiO_2).

fractional crystallization of this complex very complicated, and the purity of the bulk product does not allow exact determination of the analytical composition. Moreover, the simultaneous presence of two anions in the single crystal phase turns fitting analytical data unequivocally into a very difficult task. We studied solutions of several crystals of **2**, picked up manually, with ESI-MS, and always found two overlapping series of anions: $[CH_3OH + V_4Nb_{24}O_{76} + xK + yH]^{3-}$, $[H_2O + V_4Nb_{24}O_{76} + xNa + yH]^{3-}$, $[H_2O + V_3Nb_{24}O_{76} + xK + yH]^{3-}$, $[CH_3OH + V_3Nb_{24}O_{76} + xK + yH]^{3-}$, $[H_2O + V_3Nb_{24}O_{76} + xNa + yH]^{3-}$ (see Table S5, Figure S4). These data confirm the individuality of $[V_4Nb_{24}O_{76}]^{12-}$ and $[V_3Nb_{24}O_{76}]^{17-}$ present in **2**.

In the ^{51}V MASS NMR, there is a set of signals centered at −530 ppm (Figure 8). In solution, they merge into a single line at −532 ppm (150 Hz width), due to the quadrupolar nature of the ^{51}V nucleus.

In the Raman spectra of **1** and **2**, there are sets of Nb−O and V−O vibrations (Figure S5): 1065 (m), 913(vs), 856(s), 368 (m), 250(m), 215 (m) for **1** and 1065 (m), 935(vs), 919(s), 907(s), 867 (m), 647 (m), 498 (m), 360 (m), 329 (m), 244 (m), 211 (m) for **2**. The bands at 1065 cm^{-1} can be assigned to the tetrahedral VO_4 units. The strong bands at 913 (**1**) and 935 (**2**) cm^{-1} should correspond to terminal Nb═O groups. The Nb−O−Nb bridges appear below 900 cm^{-1}, as can be expected from the comparison with the Raman spectra of $ANbO_3$ (the highest frequency Nb−O bands at 876 cm^{-1} (for Li^+), 800 cm^{-1} (for Na^+), 832 cm^{-1} (for K^+)).[31] In $CaNb_2O_6$, the Nb−O band appears at 904 cm^{-1}, and in $AlNbO_4$ at 932 cm^{-1}.[31]

CONCLUSION

This research demonstrates rich synthetic possibilities of thermal rearrangements of hexaniobate, which, depending on the cationic composition of the reaction mixture, can follow different pathways. In the case of sodium, we isolated $Na_9H_4[VNb_{12}O_{40}\{NbO(CO_3)\}_2]\cdot 34H_2O$ consisting of a bicapped α-Keggin-type V-centered polyoxoniobate. In water, it equilibrates with vanadododecaniobate and polymeric forms by a process involving the loss of coordinated carbonate, one or two $\{NbO\}^{3+}$ caps, and oligomerization by their transformation into $\{Nb_2O_2\}^{6+}$ linkers. In the presence of potassium, we isolated a solid phase containing two unique $[V_4Nb_{24}O_{76}]^{12-}$ and $[V_3Nb_{24}O_{76}]^{17-}$ anions with the topology of a trigonal pyramid. These PONb have a hybrid metal-oxo backbone consisting of a fragment of the Keggin structure fused with pentagonal $\{NbNb_5\}$ building blocks, arranged around a central tetrahedral cavity. The cavity is occupied by three or four V^{5+} ions. In this way, $[V_4Nb_{24}O_{76}]^{12-}$ can be regarded as a polyniobate assembled around V_4O_{10} as template—a molecular analogue of P_4O_{10}, unknown in the free state, but stabilized when trapped into PONb. $[V_3Nb_{24}O_{76}]^{17-}$ can be similarly regarded as incorporating cyclic trivanadate $[V_3O_9]^{3-}$, which has negligible contribution to the equilibria in the solutions of free vanadates. In this work, we have also demonstrated remarkable tendency of a cyclic $\{K@(NbO_6)_6\}$ building block to assemble at higher temperatures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b02108.

Additional structural information, ESI(−)-MS data, and Raman spectra (PDF)
Crystallographic data for **1** (CIF)
Crystallographic data for **2** (CIF)

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Notes

The authors declare no competing financial interest.

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