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ORIGINAL PAPER

Formation of Silicon-Containing Polyoxoniobates from Hexaniobate Under High Temperature Conditions

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Abstract Hydrothermal reaction of $K_7H[Nb_6O_{19}]\cdot 13H_2O$ with $Na_2SiO_3\cdot 9H_2O$ (220 °C, 24 h) produces a lacunary siliconiobate $[Si_4Nb_{16}O_{56}]^{16-}$, which was isolated as mixed salt $NaK_8H_6[Na@Si_4Nb_{16}O_{56}]\cdot 26H_2O$ (**1**). Changing the silicon source to $Ph_2Si(OH)_2$ under the same conditions slightly improves the yield of $[Si_4Nb_{16}O_{56}]^{16-}$, which was isolated as $K_{14}H[K@Si_4Nb_{16}O_{56}]\cdot 26H_2O$ (**2**). Extending the reaction time leads to rearrangement of $[Si_4Nb_{16}O_{56}]^{16-}$ into Keggin-type silicododecaniobate $[SiNb_{12}O_{40}]^{16-}$, which was isolated and characterized as $K_8H_2(Nb_2O_2)[SiNb_{12}O_{40}]\cdot 20H_2O$ (**3**). The complexes were characterized by X-ray single crystal analysis, elemental analysis, thermogravimetry, ^{29}Si NMR.

Keywords Polyoxoniobate · Silicon · X-ray structure · Hydrothermal reactions

Introduction

The first heteropolyniobate to be reported was the one-dimensional $K_{12}(Ti_2O_2)[SiNb_{12}O_{40}]\cdot 16H_2O$, which features α-Keggin $[SiNb_{12}O_{40}]^{16-}$ ions linked together by $\{Ti_2O_2\}^{4+}$ bridges [1]. Another type of siliconiobate, a lacunary $[Si_4Nb_{16}O_{56}]^{16-}$, was found in $Na_{14}[H_2Si_4Nb_{16}O_{56}]\cdot 45.5H_2O$, which grows as large colorless single crystals when Nb_2O_5 is heated with tetraethoxysilane at 220 °C.

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The preparation of these two complexes has marked the starting point in the rediscovery of the polyoxoniobate (PONb) and tantalate (POTa) chemistry. After this initial report, many other heteropolyniobates with various tetrahedral building blocks were discovered [2, 3]. The polyoxoniobates perform well as photocatalysts for water splitting process [4] and as precursors for thin film production [5, 6], in practical point of view. From the academic viewpoint, the potentially rich chemistry of heteropolyoxoniobates and especially that of polyoxotantalates is still poorly studied and understood [2, 3]. Recently we reported coordination-induced dimerization of the Nb and Ta hexametalates [7], and a unique solubility of alkali metal salts of hybrid organometallic—PONb/POTa complexes in methanol [8]. In this research we focus upon the formation of siliconiobates and their interconversions.

Experimental Section

General Information

$K_7H[Nb_6O_{19}]\cdot 13H_2O$ was prepared as described in literature [9]. All other reagents were of commercial quality (Sigma Aldrich) and used as purchased. IR spectra were recorded on a Vertex 80 FTIR spectrometer (KBr, 4000–400 cm^{-1}). ^{29}Si NMR spectra were run on a Bruker Avance III 500 spectrometer. 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.

Synthesis

$NaK_8H_6[Na@Nb_{16}Si_4O_{56}]\cdot 26H_2O$ (1)

Solid $K_7H[Nb_6O_{19}]\cdot 13H_2O$ (5.0 g, 0.7 mmol) was dissolved in 100 mL of distilled water, then 1.57 g (1.2 mmol) of $Na_2SiO_3\cdot 9H_2O$ was added to the clear solution. After that the mixture was transferred to a stainless steel autoclave which was kept at 220 °C for 10 h. After cooling to room temperature a white precipitate was filtered off and the filtrate was placed in a jar filled with EtOH vapors. Needle-like crystals were collected after 2 days, rinsed with distilled water and vacuum-dried. Yield 1.4 g (32% based on Nb). ICP-AES found Na, K, Nb, Si (%): 1.2, 9.6, 44.7, 3.0; calculated for **1** Na, K, Nb, Si (%): 1.4, 9.4, 44.5, 3.4. IR (KBr, 1400–400 cm^{-1}): 1030(m), 1009(m), 988(w), 930(m), 905(m), 795(s), 727(m), 694(m), 584(m), 554(m), 503(m), 476(m), 455(m), 419(m). TGA: weight loss corresponds to 25($\pm$1) water molecules for a dried sample.

$K_{14}H[K@Nb_{16}Si_4O_{56}]\cdot 26H_2O$ (2)

Solid $K_7H[Nb_6O_{19}]\cdot 13H_2O$ (1.0 g, 0.7 mmol) was dissolved in 20 mL of distilled water and transferred into the Teflon cartridge of a stainless steel autoclave ($V = 30$ mL). After addition of 0.3 g (1.4 mmol) $Ph_2Si(OH)_2$ to the solution it was locked and kept at 220 °C for 10 h. After cooling a white precipitate was filtered off and the filtrate was placed into EtOH vapors. Needle-like crystals were collected after 2 days, rinsed with distilled water and vacuum-dried. Yield 0.626 g (68% based on Nb). ICP-AES found K, Nb, Si (%): 15.6, 41.6, 2.9; calculated for **2** K, Nb, Si (%): 15.4, 41.9, 3.2.

IR (KBr, 1400–400 cm^{-1}): 1032(s); 983(s); 930(s); 870(s); 812(s); 789(s); 727(s); 700(s); 586(s); 548(s); 505(s); 484(s). TGA found 26(±1) water molecules for a dried sample.

$K_8H_2(Nb_2O_2)[SiNb_{12}O_{40}]\cdot 20H_2O$ (3)

Solid $K_7H[Nb_6O_{19}]\cdot 13H_2O$ (1.0 g, 0.7 mmol) was dissolved in 20 mL of distilled water and transferred into the Teflon cartridge of stainless steel autoclave (V = 30 mL). After addition of 0.3 g (1.4 mmol) of $Ph_2Si(OH)_2$ to the solution it was kept at 220 °C for 4 days. After cooling a white precipitate was filtered off and the filtrate was placed into EtOH vapors. A mixture of needle-like (**2**) and polyhedral (**3**) crystals were found in 2 days. The polyhedral crystals were separated manually identified as $K_8H_2(Nb_2O_2)[SiNb_{12}O_{40}]\cdot 20H_2O$ (**3**) by X-ray diffraction. The reproducible yield is about 40%. IR (1400–400, KBr, cm^{-1}): 1174 (m), 1045 (s), 942(m), 874(w), 800(w), 734(w), 640(w), 621(w), 446(m).

Crystallography

The diffraction data for **1** and **2** were collected on a Bruker X8Apex-II CCD diffractometer at 100 K, and the data for **3** on a Bruker Apex Duo at 160 K with MoKα radiation ($\lambda = 0.71073$ Å) by doing ω and φ scans of narrow (0.5°) frames. All three structures were solved by direct methods and refined by full-matrix least-squares treatment against $|F|^2$ in anisotropic approximation with SHELX 2014/7 in ShelXle program [10]. Absorption corrections were applied empirically with SADABS [11]. Crystallographic data and refinement details are given in Table 1. The main geometrical parameters are summarized in Table 2. Further details may be obtained from the ICSD (Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD 431691 (**1**), 431692 (**2**), 431693 (**3**).

Results and Discussion

The first entry into the chemistry of heteropolyniobates (PONb) has been achieved by thermolysis of Nb_2O_5 in the presence of a convenient heteroelement source under highly basic conditions at 200–220 °C [1]. In this way unprecedented Keggin-type PONb $[XNb_{12}O_{40}]^{n-}$ were isolated and structurally characterized. These anions are, as a rule, connected together by $(M_2O_2)^{n+}$ (M = Nb, Ti) bridges: the examples are $K_{12}(Ti_2O_2)[SiNb_{12}O_{40}]\cdot 16H_2O$ [1], $Na_{12}(Ti_2O_2)[TNb_{12}O_{40}]\cdot xH_2O$ and $Na_{10}(Nb_2O_2)[TNb_{12}O_{40}]\cdot xH_2O$ (T = Si, Ge) [12], $K_{10}(Nb_2O_2)[GeNb_{12}O_{40}]\cdot 11H_2O$ [13]. Other examples are non-bridged PONb with Keggin structure:

Table 1 Experimental details

	1	2	3
Chemical formula	$H_{58}K_8Na_2Nb_{16}O_{82}Si_4$	$H_{53}K_{15}Nb_{16}O_{82}Si_4$	$H_{42}K_8Nb_{14}O_{62}Si$
M_r	3328.16	3550.84	2675.96
Crystal system, space group	Triclinic, $\bar{P}1$	Triclinic, $\bar{P}1$	Orthorhombic, *Immm*
Temperature (K)	100	100	160
a, b, c (Å)	16.3181 (11), 23.7443 (18), 24.1735 (17)	12.0354 (2), 15.3207 (3), 22.4737 (5)	10.8890 (11), 11.6390 (13), 19.530 (3)
α, β, γ (°)	98.923 (2), 101.940 (2), 106.275 (2)	91.988 (1), 90.879 (1), 98.581 (1)	90, 90, 90
V (Å^3)	8567.0 (11)	4094.21 (14)	2475.2 (5)
Z	4	2	2
μ (mm^{-1})	2.63	3.10	3.96
Crystal size (mm)	0.20 × 0.08 × 0.05	0.25 × 0.10 × 0.02	0.05 × 0.04 × 0.03
Diffractometer	Bruker X8Apex	Bruker X8Apex	Bruker Apex Duo
T_{min}, T_{max}	0.467, 0.745	0.587, 0.746	0.469, 0.745
No. of measured, independent and observed [$I > 2$ s(I)] reflections	66,129, 33,028, 17,399	45,151, 18,965, 16,427	5204, 1421, 950
R_{int}	0.074	0.034	0.053
(sin θ/λ)$_{max}$ (Å^{-1})	0.627	0.654	0.625
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.083, 0.263, 1.00	0.038, 0.099, 1.02	0.066, 0.189, 1.07
No. of reflections, parameters, restraints	33,028, 1943, 84	18,965, 1066, 0	1421, 119, 0
	$w = 1/[\sigma^2(F_o^2) + (0.1412P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0279P)^2 + 47.9397P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0976P)^2 + 60.4564P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.68, −2.09	2.29, −2.43	2.27, −2.14

Computer programs: *APEX2* (Bruker-AXS, 2004), *SAINT* (Bruker-AXS, 2004), *SHELXS2014* (Sheldrick, 2014), *SHELXL2014*/7 (Sheldrick, 2014), ShelXle (Hübschle, 2011)

$Na_{16}[TNb_{12}O_{40}]\cdot4H_2O$ (T=Si, Ge) [14] and $Li_{13}K[SiNb_{12}(OH)_2O_{38}]\cdot17H_2O$ [15]. Non-conventional lacunary PONb were found in $Na_{14}[H_2Si_4Nb_{16}O_{56}]\cdot45.5H_2O$ [1] and $Na_{15}[(PO_2)_3PNb_9O_{34}]\cdot22H_2O$ [16], whose structures can not be simply derived from the Keggin type dodecaniobates.

In the case of siliconiobates M. Nyman and coworkers used high temperature solvation of hydrated niobium oxide in the presence of a base and tetraethoxysilane [2, 3]. In the present work we have found that heating of $K_7H[Nb_6O_{19}]\cdot13H_2O$ with $Na_2SiO_3\cdot9H_2O$ or even $Ph_2Si(OH)_2$ under hydrothermal conditions at 220 °C for 10 h gives lacunary tetrasilicohexakaidekaniobate polyoxoanion $[Si_4Nb_{16}O_{56}]^{16-}$ in acceptable yields. Both reaction solutions (with silicate and silanediol) have only two signals in ^{29}Si NMR spectra, which correspond to $[Si_4Nb_{16}O_{56}]^{16-}$, with the same chemical shifts as reported [1]. Prolonged heating of the reaction mixture leads to rearrangement of the lacunary structure into closed α-Keggin anion $[SiNb_{12}O_{40}]^{16-}$, which was isolated and characterized as $K_8H_2(Nb_2O_2)[SiNb_{12}O_{40}]\cdot20H_2O$, in the reaction with the silanediol. Apparently, the harsh reaction conditions cause cleavage of the Si–C bonds releasing the silicate. According to ^{29}Si NMR, is only two signals at −78 and −79 ppm, which is close to −78.5; −79.3 ppm reported by M. Nyman [1]. In aqueous solution highly charged $[SiNb_{12}O_{40}]^{16-}$ anions can be stabilized by reducing their charge by association with alkali metal cations and/or by coordination with two $\{NbO\}^{3+}$ "caps" similarly to the formation of the well-known phosphovanadate $[PV_{14}O_{42}]^{9-}$ from $[PV_{12}O_{40}]^{16-}$ and two VO^{3+} [17]. This stabilization is also found in the solutions of Keggin-based germanoniobates $Rb_{13}[GeNb_{13}O_{41}]\cdot23H_2O$ and $Cs_{10.6}[H_{2.4}GeNb_{13}O_{41}]\cdot27H_2O$. Small Angle X-ray Scattering studies of solutions of the first two salts in revealed oligomerization of the monomers into chain-like structures, the extent of oligomerization being controlled by pH, concentration, and the counterion. Chains of up to six Keggin ions in solution, with the large alkali cations for charge-balance were observed [18].

The crystal structure of **1** consists of $[Si_4Nb_{16}O_{56}]^{16-}$ anions connected with solvated sodium and potassium cations. The anion has four Si atoms of two types: two inner silicon atoms (type 1) connected by oxygen ligand [d(Si1–O108) = 1.666(13) Å, d(Si2–O108) = 1.648(12) Å] into a pyrosilicate $\{Si_2O_7\}$ fragment, which is typical for silicates. Each of the two outer silicon atoms (type 2) has a terminal oxygen ligand [d(Si45–O9) = 1.669(13) Å, d(Si48–O2) = 1.632(12) Å]. The longer Si–O distances possibly indicate the formation of Si–OH bonds. These two types of Si atoms correspond to two signals in ^{29}Si NMR, observed in the solutions of $[Si_4Nb_{16}O_{56}]^{16-}$. There are two independent polyanions in the unit cell, the main difference between these units being the coordination number of the sodium cations trapped into the lacuna. One Na^+ has CN 5 (four oxygens from PONb plus one water molecule), and another has CN 6 with two coordinated water molecules (Fig. 1). In both cases the Na–O distances lie in the expected interval 2.29(2)–2.49(2) Å, defined by the sum of the ionic radii of Na^+ and O^{2-} with a certain degree of flexibility. It is the first example of Na^+ inclusion into the cavity of $[Si_4Nb_{16}O_{56}]^{16-}$ and also indication that in a strong competition between sodium and potassium cations sodium is more preferable to enter the lacuna in $[Si_4Nb_{16}O_{56}]^{16-}$.

Table 2 Selected geometric parameters (Å)

Complex **1**			
Si1–O107	1.594 (12)	Si43–O80	1.590 (13)
Si1–O108	1.666 (13)	Si43–O92	1.626 (13)
Si1–O109	1.664 (12)	Si43–O101	1.649 (11)
Si1–O111	1.662 (11)	Si43–O121	1.640 (12)
Si2–O108	1.648 (12)	Si45–O9	1.669 (13)
Si2–O110	1.645 (11)	Si45–O27	1.617 (12)
Si2–O112	1.673 (12)	Si45–O32	1.621 (12)
Si2–O114	1.612 (13)	Si45–O42	1.631 (11)
Si3–O120	1.575 (13)	Si48–O2	1.632 (12)
Si3–O122	1.655 (13)	Si48–O23	1.610 (13)
Si3–O123	1.645 (12)	Si48–O24	1.648 (13)
Si3–O127	1.654 (12)	Si48–O28	1.588 (15)
Si4–O124	1.654 (13)	Si49–O66	1.636 (18)
Si4–O125	1.622 (12)	Si49–O96	1.661 (12)
Si4–O126	1.640 (11)	Si49–O103	1.622 (13)
Si4–O127	1.650 (12)	Si49–O104	1.593 (14)
Complex **2**			
Si1X–O28	1.652 (4)	Si2X–O40	1.616 (4)
Si1X–O30	1.651 (4)	Si2X–O45	1.609 (4)
Si1X–O36	1.606 (4)	Si2X–O48	1.643 (4)
Si1X–O37	1.605 (4)	Si2–O20	1.651 (4)
Si1–O23	1.612 (4)	Si2–O33	1.657 (4)
Si1–O24	1.655 (4)	Si2–O51	1.614 (4)
Si1–O32	1.656 (4)	Si2–O53	1.641 (4)
Si1–O53	1.637 (4)	O2W–Si2X$^{\mathrm{ii}}$	1.656 (4)
Si2X–O2W$^{\mathrm{i}}$	1.656 (4)		
Complex **3**			
Si1–O5$^{\mathrm{iii}}$	1.639 (14)	Si1–O5$^{\mathrm{vii}}$	1.639 (14)
Si1–O5$^{\mathrm{iv}}$	1.639 (14)	Si1–O5$^{\mathrm{viii}}$	1.639 (14)
Si1–O5$^{\mathrm{v}}$	1.639 (14)	Si1–O5$^{\mathrm{ix}}$	1.639 (14)
Si1–O5$^{\mathrm{vi}}$	1.639 (14)	Si1–O5	1.639 (14)

Symmetry code(s): (i) $x + 1, y, z$; (ii) $x - 1, y, z$; (iii) $-x, y, z$; (iv) $x, -y + 1, -z + 1$; (v) $x, y, -z + 1$; (vi) $-x, -y + 1, z$; (vii) $-x, -y + 1, -z + 1$; (viii) $-x, y, -z + 1$; (ix) $x, -y + 1, z$

Crystal structure of **2** is built of the same $[Si_4Nb_{16}O_{56}]^{16-}$ polyoxoniobate anions which are connected with solvated potassium cations. The terminal Si–O distances for the type 2 outer silicon atoms are elongated, Si2X–O2 W 1.656(4) Å and Si1X–O28 1.652(4) Å, which means that two additional protons that are needed for the charge balance are located on these oxygens, thus forming $[(SiOH)_2Si_2Nb_{16}O_{54}]^{14-}$. In the case of **2** the cavity is occupied with a potassium cation (Fig. 2), which has CN 8: $d(K–O^{Nb}) = 2.748(4)–2.817(4)$ Å; $d(K–O^{w}) = 2.794(12)–3.140(6)$ Å.

In the crystal structure of **3** α-Keggin type anions $[SiNb_{12}O_{40}]^{16-}$ combine into infinite linear chains through additional Nb–O groups, like in the known structures of $K_{12}(Ti_2O_2)[SiNb_{12}O_{40}]\cdot 16H_2O$ [1] or $Na_{10}(Nb_2O_2)[SiNb_{12}O_{40}]\cdot xH_2O$ [12] (Fig. 3).

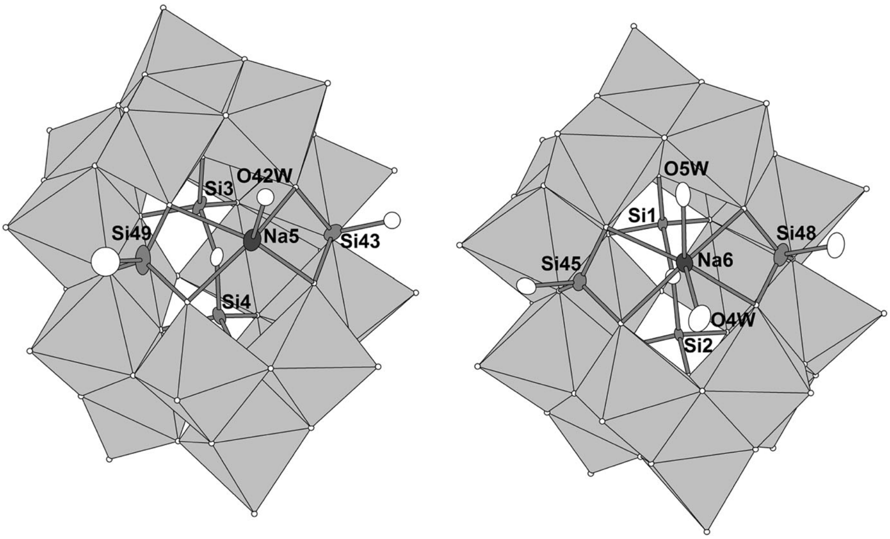

Fig. 1 Inclusion of Na^+ into lacunary type $[Si_4Nb_{16}O_{56}]^{16-}$ (thermal ellipsoids 50% probability). Two different types of sodium coordination spheres in the crystal structure of **1**

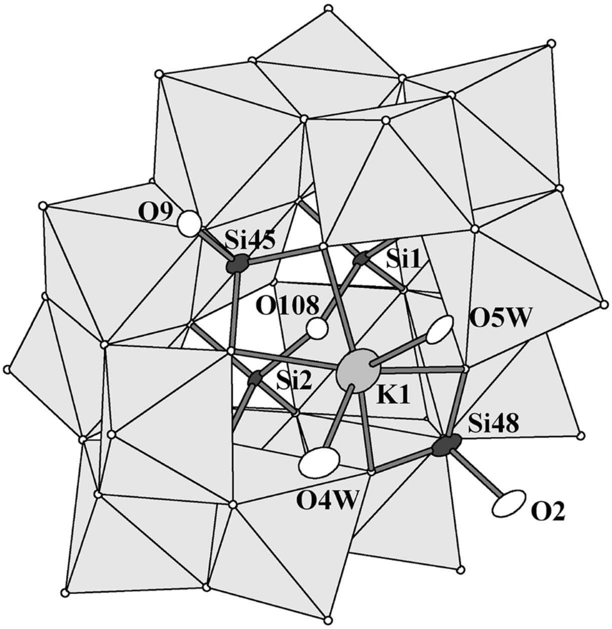

Fig. 2 The structure of lacunary type $[Si_4Nb_{16}O_{56}]^{16-}$ (thermal ellipsoids 50% probability) in **2**. In the crystal structure the vacancy is occupied with potassium cation

The main difference between the two reported structures and **3** are in the number of cations, since in **3** only eight K^+ cations were found. Moreover, inside the polymeric chains the individual anions $[SiNb_{12}O_{40}]^{16-}$ can rotate by 180 °

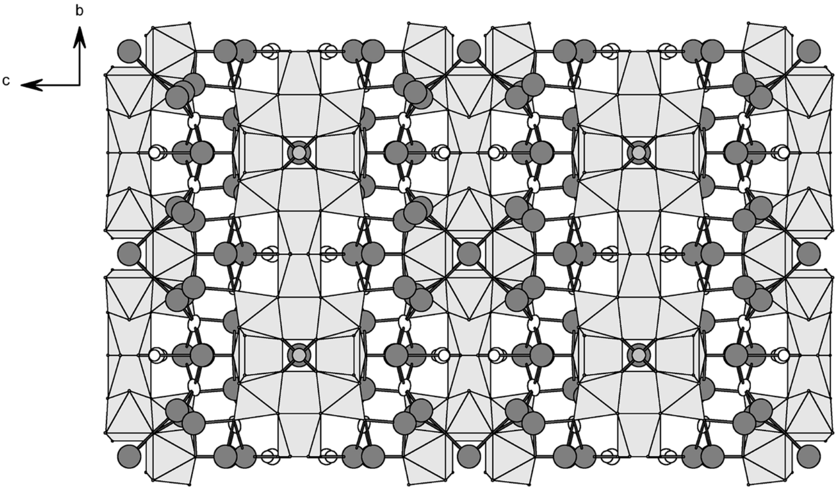

Fig. 3 The infinite chains of disordered Keggin type $[SiNb_{12}O_{40}]^{16-}$ anions with $[Nb_2O_2]^{6+}$ bridges along [010] crystal direction

producing total disorder of 52 polyoxoanion atoms (12Nb + 40O) over two alternative positions and, additionally, the $[Nb_2O_2]^{6+}$ bridges can be disordered over four positions. These two alternative orientations of the anion leave only the silicon atom in the same place regardless of the orientation (Fig. 4).

All this consideration mean that in a single linear chain there are four different possibilities of connection between $[SiNb_{12}O_{40}]^{16-}$ anions. Rotation of the Keggin

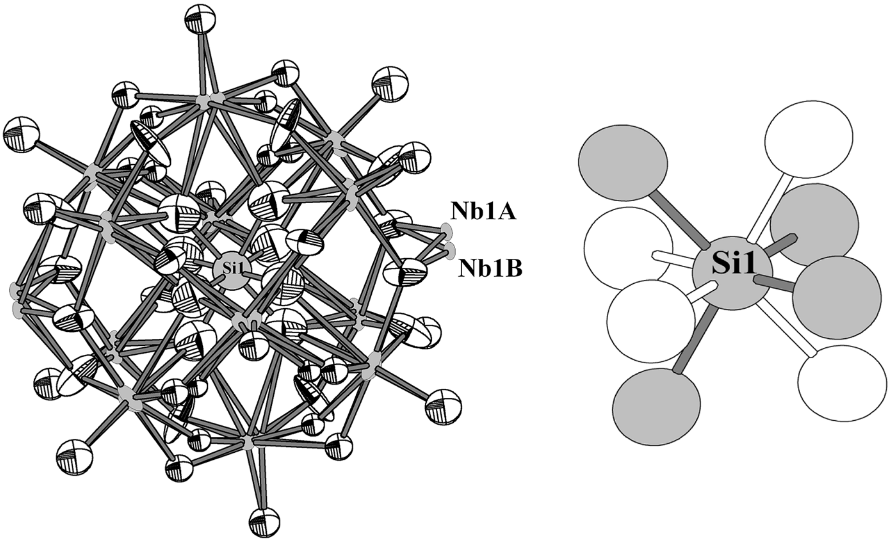

Fig. 4 Orientation disordering of $[SiNb_{12}O_{40}]^{16-}$ anions in the crystal structure of **3** (*left*); two orientations of $\{SiO_4\}$ with mutual silicon atom (*right*)

anions was found in $Na_{16}[SiNb_{12}O_{40}]\cdot4H_2O$, which has two signals at −72.4 and −74.1 ppm in solid state ^{29}Si NMR from two crystallographically independent silicon atoms [14]. Contrary to **3**, $K_{12}(Ti_2O_2)[SiNb_{12}O_{40}]\cdot16H_2O$ and $Na_{10}(Nb_2O_2)[SiNb_{12}O_{40}]\cdot xH2O$, which contain linear chains, $K_{10}[Nb_2O_2(H_2O)_2][SiNb_{12}O_{40}]\cdot12H_2O$ is composed of anionic zigzag chains formed by $[SiNb_{12}O_{40}]^{16-}$–Keggin clusters linked together via bridging $[Nb_2O_2(H_2O)_2]^{6+}$ units. These zigzag chains pack parallel to the *ab* plane, and the chains between two neighboring layers along the *c* axis run perpendicular to each other [19].

Conclusion

In this paper we successfully tested two new silicon sources for producing of silicon-containing polyoxoniobates. In the case of $Ph_2Si(OH)_2$ the yield of lacunary type anion $[Si_4Nb_{16}O_{56}]^{16-}$ was found to be slightly better in comparison with $Na_2SiO_3\cdot9H_2O$ or previously reported $Si(OEt)_4$. We have found rearrangement of the lacunary anion into α-Keggin anion during prolonged heating of the reaction mixture. The lacunary anion $[Si_4Nb_{16}O_{56}]^{16-}$ can coordinate both Na^+ and K^+ with a marked preference for Na^+.

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