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Cupric Siliconiobate. Synthesis and Solid-State Studies of a Pseudosandwich-Type Heteropolyanion

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The Na^+ and $[Cu(en)_2(H_2O)_2]^{2+}$ (en = ethylenediamine) salt of a pseudosandwich-type heteropolyniobate forms upon prolonged heating of $Cu(NO_3)_2$ and hydrated $Na_{14}[(SiOH)_2Si_2Nb_{16}O_{54}]$ in a mixed water−en solution. The structure [$a = 14.992(2)$ Å, $b = 25.426(4)$ Å, $c = 30.046(4)$ Å, orthorhombic, *Pnn*2, R1 = 6.04%, based on 25869 unique reflections] consists of two $[Na(SiOH)_2Si_2Nb_{16}O_{54}]^{13-}$ units linked by six sodium cations, and this sandwich is charge-balanced by five $[Cu(en)_2(H_2O)_2]^{2+}$ complexes, seven protons, and three additional sodium atoms (all per a sandwich-type cluster). Diffuse-reflectance UV−vis indicates that there is a λ_{max} at 383 nm for the Cu^{II} d−d transition and the ^{29}Si MAS NMR spectrum has two peaks at −78.2 ppm (151 Hz) and −75.5 ppm (257 Hz) for the two pairs of symmetry-equivalent internal $[SiO_4]^{4-}$ and external $[SiO_3(OH)]^{3-}$ tetrahedra, respectively. Unlike tungsten-based sandwich-type complexes, the $[Na(SiOH)_2Si_2Nb_{16}O_{54}]^{13-}$ units are linked exclusively by Na^+ instead of one or more d-electron metals.

Introduction

Fundamental and applied studies of niobium oxide molecules and materials continue to grow unabated.[1] The $[Nb_6O_{19}]^{8-}$ Lindqvist ion is at the center of much of this ongoing research[2–23] because it is the dominant species of basic (pH > 7) niobium oxide solutions.[2–8] Alkali salts of $[Nb_6O_{19}]^{8-}$ are readily synthesized and crystallized by the dissolution of hydrous niobium oxide into 1−5 M solutions of AOH (A = Na, K, Rb, or Cs).[9,10] In contrast, isolation of

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(23) Recent studies have shown that $[Cu(L)_n]^{2+}$ (L = en or H_2O) cations afford crystalline derivatives of large isopolyniobate assemblies, including supramolecular aggregates of $[Nb_7O_{22}]^{9-}$ and $[Cu(L)_2]^{2+}$. For more information, see: (a) Bontchev, R. P.; Nyman, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 6670–6672. (b) Niu, J.; Ma, P.; Niu, H.; Li, J.; Zhao, J.; Song, Y.; Wang, J. *Chem.—Eur. J.* **2007**, *13*, 8739–8748.

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heteropolyniobates[24–31] requires less alkaline solutions and higher processing temperatures (hydrothermal conditions). Previously, we have prepared the α-$[XNb_{12}O_{40}]^{16-}$ (X = Si or Ge) Keggin anion linked by $[Ti_2O_2]^{4+}$ or $[Nb_2O_2]^{6+}$ as sodium or potassium salts and as isolated clusters charge-balanced by lithium or sodium.[24–26,28–30] In addition, two heteropolyniobates, $[(SiOH)_2Si_2Nb_{16}O_{54}]^{14-}$ and $[(PO_2)_3PNb_9O_{34}]^{15-}$, that are lacunary derivatives of the α-Keggin ion have been crystallized as sodium salts.[24,27]

To even begin to approach the rich diversity of the related polyoxometalate chemistry of tungsten, molybdenum, and vanadium,[32] the reactions of polyoxoniobates with transition-metal complexes must be more extensively explored. Reports have shown that alkali salts of $[Nb_6O_{19}]^{8-}$ react with transition-metal complexes soluble in basic media to produce charge-balanced, decorated, and linked phases.[11–23] The lithium and sodium salts of α-$[XNb_{12}O_{40}]^{16-}$ have limited solubility in water,[25,29] but the lacunary derivative, $[(SiOH)_2Si_2Nb_{16}O_{54}]^{14-}$, is readily dissolved and recrystallized.[24] This also indicates that the compound is stable in an aqueous solution and suggests that it warrants further investigation to determine its reactivity with d- or f-electron metals.

We now report the synthesis of $[Cu(en)_2(H_2O)_2]_5Na_9[Na(SiOH)_2Si_2Nb_{16}H_{3.5}O_{54}]_2\cdot 25H_2O$ (**1**) from the prolonged heating of $Cu(NO_3)_2$ and hydrated $Na_{14}[(SiOH)_2Si_2Nb_{16}O_{54}]$ (**2**) in a mixed water−en (en = ethylenediamine) solution. The structure of **1**, determined by single-crystal X-ray diffraction analysis, consists of two $[Na(SiOH)_2Si_2Nb_{16}O_{56}]^{13-}$ units linked by six sodium cations to form a pseudosandwich-type compound that is charge-balanced by five $[Cu(en)_2(H_2O)_2]^{2+}$ complexes, seven protons, and three additional sodium atoms (all per sandwich-type cluster). Complete characterization of this complex by elemental (and thermogravimetric) analysis, FT-IR, diffuse-reflectance UV−vis, and ^{29}Si MAS NMR spectroscopy clearly defines its structural and electronic properties.

Experimental Section

General Methods and Materials. $Cu(NO_3)_2\cdot 2.5H_2O$ (certified ACS), HCl (certified ACS Plus), NaOH (ACS grade), and KOH (ACS grade) were purchased from Fisher. Ethylenediamine (en, $NH_2CH_2CH_2NH_2$; ReagentPlus ≥99%) and $Si(OC_2H_5)_4$ (98%) were purchased from Aldrich. Amorphous hydrous Nb_2O_5 was obtained from Reference Metals, Inc. Elemental analysis (Cu, Na, Nb, and Si) was performed by Galbraith Laboratories, Inc. Thermal analysis was performed with a TA Instruments SDT 2960 for simultaneous thermogravimetric and differential thermal analysis (TGA-DTA) under a N_2 flow with a heating rate of 10 °C/min. Infrared spectra (4000−400 cm^{-1}) were recorded on a Thermo Nicolet 380 FT-IR equipped with a Smart Orbit (Diamond) ATR accessory. Diffuse-reflectance spectra (300−800 nm) were collected on a Shimadzu UV-3600 UV−vis−NIR. The system operates with an integrating sphere of 150 mm inner diameter and is equipped with a photomultiplier and a PbS cell. All reflectance values are referenced to $BaSO_4$ (100% reflectance). The sample of $Cu(en)_2(NO_3)_2$ was prepared by dissolving 0.5 g of $Cu(NO_3)_2\cdot 2.5H_2O$ in 10 g of CH_3OH and adding en until a purple precipitate formed. The solid was identified by infrared spectroscopy and by matching its powder X-ray pattern with two reported structures.[33,34] Solid-state ^{29}Si MAS NMR spectra were obtained at 79.5 MHz on a Bruker Avance 400 using a 4 mm broad-band probe spinning at 4 kHz, standard single-pulse Bloch decay and CPMAS pulse sequences, and high-power ^{1}H TPPM decoupling. To obtain quantitative integration, a recycle delay of 480 s for the direct spectra was used. The ^{29}Si NMR chemical shifts were referenced to the external secondary standard Q_8M_8 ($\delta = +11.5$ ppm with respect to TMS $\delta = 0$ ppm).

Synthesis of $[Cu(en)_2(H_2O)_2]_5Na_9[Na(SiOH)_2Si_2Nb_{16}H_{3.5}O_{54}]_2\cdot 25H_2O$ (1). A 0.13 g sample of $Cu(NO_3)_2\cdot 2.5H_2O$ (0.56 mmol) was dissolved in 3 mL of H_2O, and 4 g of en (66 mmol) was added to 3 mL of H_2O in a separate container. The $Cu(NO_3)_2$ solution was added to the H_2O−en mixture, and the resulting solution was added dropwise to a 0.30 g sample of **2** (0.08 mmol) dissolved in 5 mL of H_2O. The mixture of $Cu(NO_3)_2$, H_2O−en, and **2** was vigorously stirred and heated at ~100 °C until the volume was reduced by 50% and a significant amount of precipitate had formed. The precipitate was cooled to ~60 °C, and 1 mL of 6 M HCl was slowly added dropwise with continuous stirring. The resulting clear solution was again heated to boiling and concentrated to a total volume of 8 mL (the temperature gradually increased to ~110 °C because of the lower ratio of H_2O to en upon evaporation). The solution was syringe-filtered (0.45 μm) warm, cooled to room temperature, and allowed to slowly evaporate in air. After 3 days, 0.26 g (0.04 mmol, ~99.5% yield based on **2**) of the product was collected by suction filtration, washed with CH_3OH, and dried in vacuo. IR (1100−525 cm^{-1}): 1053 (m), 998 (s), 919 (s), 841 (s), 760 (w, sh), 715 (w, sh), 653 (s), and 539 (m). ^{29}Si MAS NMR: $\delta = -75.5$ ppm (257 Hz) and -78.2 ppm (151 Hz). Anal. Calcd for $N_{20}O_{147}Na_{11}Nb_{32}Cu_5Si_8C_{20}H_{161}$ (MW = 6796 g/mol): Cu, 4.7; Na, 3.7; Nb, 44; H_2O, 9.3; Si, 3.5. Found: Cu, 4.4; Na, 3.3; Nb, 42; H_2O, 9.1; Si, 3.4.

Synthesis of $Na_{14}[(SiOH)_2Si_2Nb_{16}O_{54}]\cdot 45.5H_2O$ (2). The synthesis of **2** is based on a modified literature procedure.[24] A 1.62 g (7.8 mmol) sample of $Si(OC_2H_5)_4$ and 2.1 g (4.5 mmol) of $Nb_2O_5\cdot 11.25H_2O$ were added to 48 mL of 0.5 M NaOH in a 125 mL Teflon liner for a Parr reactor. The mixture was stirred for 30 min at 60 °C and placed in an oven at 180 °C for 15 h. After the sample was cooled to room temperature, the mixture was transferred to a 250 mL Erlenmeyer flask, heated to ~95 °C, and filtered hot with a 0.45 μm syringe. The solution was boiled in a 250 mL beaker until the total volume was 20−25 mL and filtered hot with a 0.45

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Table 1. Summary of Crystallographic Data and Structure Refinement for **1**

	1
empirical formula	$C_{20}H_{154}Cu_5N_{20}Na_{11}Nb_{32}O_{147}Si_8$
fw	6796.1
space group	*Pnn*2
unit cell param	$a = 14.992(2)$ Å
	$b = 25.426(4)$ Å
	$c = 30.046(4)$ Å
V	11453(3) Å^3
Z	2
T	173(2) K
d(calcd)	1.971 g cm^{-3}
λ	0.710 73 Å
μ	2.139 cm^{-1}
2θ min, max	2.1°, 56.5°
final R1^a $[I > 2\sigma(I)]$	0.0604
final wR2^b $[I > 2\sigma(I)]$	0.1768
GOF	1.104

^{a} $R1 = \sum||F_o| - |F_c||/|F_o|$. ^{b} $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

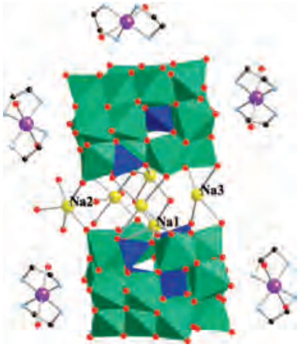

Figure 1. Combination ball-and-stick/polyhedral representation of **1**. All hydrogen atoms are omitted for clarity. The NbO_6 octahedra are shown in green, the SiO_4/$SiO_3(OH)$ tetrahedra are shown in blue, and the O, Na, C, N, and Cu atoms are shown in red, yellow, black, light blue, and purple, respectively.

μm syringe. The clear solution was cooled to ~5 °C and placed in a 125 mL Erlenmeyer flask. After 12 h, 1.7 g (0.47 mmol, 85% yield based on Nb) of a crystalline material was collected by suction filtration and dried in vacuo. IR (1100−525 cm^{-1}): 1012 (m), 1007 (m), 982 (m), 930 (m), 860 (s), 790 (w), 670 (s), and 559 (w). ^{29}Si MAS NMR: $\delta = -76.4$ ppm (156 Hz) and -77.9 ppm (86 Hz).

Crystallographic Studies of 1. Single-crystal X-ray diffraction of **1** was performed at 173 K on a Bruker AXS SMART-CCD diffractometer with graphite-monochromated Mo Kα (0.71073 Å) radiation. Data collection and reduction were carried out with *SMART 5.054* (Bruker, 1998) and *SAINT 6.02* (Bruker, 2001) software, respectively. An empirical absorption correction was applied using *SADABS* (Sheldrick, G. *SADABS*; University of Göttingen: Göttingen, Germany, 1999). All subsequent structure solution and refinement were performed within the *WinGX* system. The structure was solved by Direct Methods (program *SIR97*) and refined by full matrix least squares on F^2 (*SHELX97*). The hydrogen atoms on the en ligands (two per nitrogen and two per carbon) could not be located directly because of the motion of the rings in the lattice. Therefore, they were fixed using a riding model (HFIX command in *SHELX*). Crystallographic data are summarized in Table 1, and the complete data of atomic coordinates and bond lengths and angles are available as a CIF file in the Supporting Information.

Results

Synthesis and Structure. The reaction of hydrous Nb_2O_5 and $Si(OC_2H_5)_4$ in 0.5 M NaOH at 180 °C for 15 h gives the parent complex, $Na_{14}[(SiOH)_2Si_2Nb_{16}O_{54}]\cdot 45.5H_2O$ (**2**), in high yield (85%) and in high purity (based on ^{29}Si MAS NMR and FT-IR). This procedure was slightly modified from the literature to improve the yield (original yield 40−50%).[24] Specifically, the improvements were made by lowering the synthesis temperature by 40 °C and recrystallizing from water rather than a water−ethanol mixture. The latter process produced some amorphous product in addition to crystals of **2**. The addition of $Cu(en)_2(NO_3)_2$ to an aqueous solution of **2** failed to produce **1** at room temperature (or refluxing for 24 h) because **2** could be quantitatively recovered with partial evaporation of the solution. In a mixed H_2O and en (9:1 molar ratio) solvent system, **1** could be obtained with prolonged heating and concentration of the solution by ~50%. However, H_2O and en are now present in approximately equimolar amounts (based on the difference in their boiling points), and under these conditions, **1** and unreacted **2** start to coprecipitate (based on infrared data) because of their poor solublility in en. Complexes **1** and **2** redissolve by a *slight* increase of the H_2O−en molar ratio with the addition of 1 mL of aqueous 6 M HCl to react with some of the en present to form the $[NH_3CH_2CH_2NH_3]Cl_2$ salt. Further heating and concentration of the alkaline solution gives **1** in high yield (~99.5%) and in high purity (based on ^{29}Si MAS NMR and FT-IR). In addition, the reaction is not particularly sensitive to the amount of Cu^{II} present because **1** could be obtained from **2** with Cu^{II}−**2** ratios ranging from 4:1 to 8:1, with 7:1 giving the highest yield.

The structure of **1** was solved in the orthorhombic space group *Pnn*2, and it contains two subunits of $[Na(SiOH)_2Si_2Nb_{16}H_{3.5}O_{54}]^{9.5-}$ (**1**Na) linked by sodium atoms including two half-occupied Na3 sites and two fully occupied Na2 sites (Figure 1). The Na2 site is octahedral, with one Nb═O$_t$−Na bond (O$_t$ = terminal oxygen) to each of the two **1**Na subunits. The Na−O$_t$ bond length is 2.4 Å, and the four bonds of Na2 to O$_{water}$ range from 2.3 to 2.4 Å. The Na3 site is approximately square-planar with two bonds (Si−O$_t$−Na and Nb═O$_t$−Na) to each **1**Na subunit. These Na−O bond lengths range from 2.8 to 3.0 Å. Each subunit of **1**Na consists of two triniobium-vacant $[\alpha\text{-}SiNb_9O_{34}]^{19-}$ Keggin moieties fused by two shared NbO_6 octahedra with two surface $[SiO_3(OH)]^{3-}$ tetrahedra and a single sodium in the "pocket" (or lacunary site) of the cluster. The pocket sodium (Na1) is octahedral with four bonds (2.3−2.4 Å) to the bridging oxygen atoms of the cluster (Si−O$_b$−Nb, where O$_b$ = bridging oxygen) and two Na−O$_{water}$ bonds (also 2.3−2.4 Å). These water molecules bridge the two Na1 sites of the dimer and join the two **1**Na subunits together. There are five $[Cu(en)_2(H_2O)_2]^{2+}$ complexes, with each copper center located approximately 3.8−4.1 Å from the surface oxygen atoms of the **1**Na clusters. Bond-valence-sum (BVS) calculations confirm that the oxidation state of copper is 2+.[35] In addition, there are 3 disordered sodium cations and 25 water molecules (per Na-linked sandwich complex) located in the lattice. Elemental analysis data confirm that the ratio of Na:Cu:Si:Nb is 11:5:8:32.

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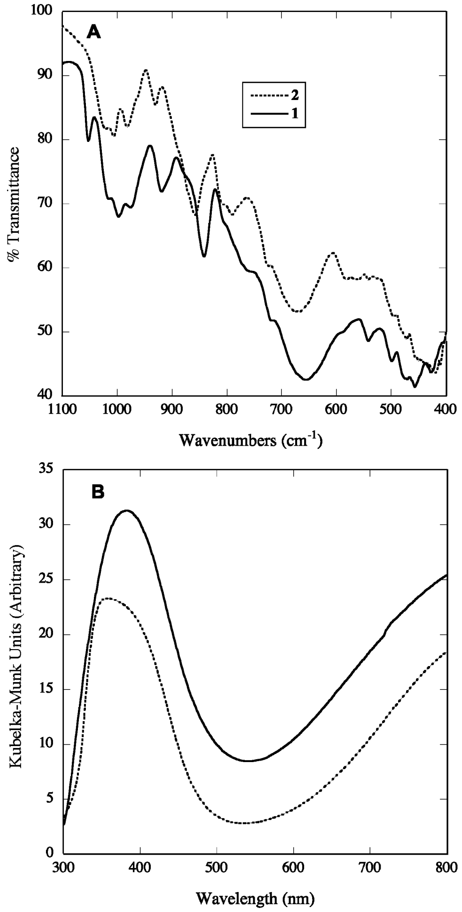

Figure 2. (A) Infrared spectra of **1** and **2**. (B) Diffuse-reflectance UV−vis spectra of $Cu(en)_2(NO_3)_2$ (dotted line) and **1** (solid line), referenced to barium sulfate (100% reflectance).

Charge-balance considerations of **1** indicate that there must be seven protons per sandwich complex. However, the high number of crystallographically independent atoms and variable parameters, low symmetry, presence of heavy atoms (Nb and Cu), and high mobility of the lattice species prevented the direct location of these protons from the Fourier maps. Furthermore, the distortion and asymmetry of the cluster does not permit the location of the protons by BVS calculations. However, the most reasonable assumption is that these charge-balancing protons are disordered over bridging μ_2-ONb_2 sites of the cluster.[36] Previous studies on $[Nb_6O_{19}]^{8-}$ indicate that the protonation of polyoxoniobates occurs, even in alkaline conditions, when a less polar solvent (such as ethanol) is added to an aqueous solution of the cluster because of the increased tendency for ion pairing between $[Nb_6O_{19}]^{8-}$ and H^+ as the dielectric constant of the solvent mixture is reduced.[10,37] Similar observations and data treatment have been reported for copper−amine complex salts of isopolyniobates.[23]

Spectroscopic Studies. The infrared spectra of **1** and **2** are shown in Figure 2A. Complex **2** displays bands attributable to Si−O(H) centered around 1000 cm^{-1} as well as bands at 930, 860, and 670 cm^{-1}, which are primarily assigned to Nb═O stretching, Nb−O stretching, and Nb−O−Nb bending, respectively.[38–41] In complex **1**, the same bands are present, but they are shifted to lower wavenumbers. This may be partially attributable to the additional protonation of the **1**Na units in **1** relative to the parent structure **2**, where only the external $[SiO_3(OH)]^{3-}$ tetrahedra are protonated. In addition, Rocchiccioli-Deltcheff and co-workers have reported that shifts to lower wavenumbers are observed with increasing electrostatic anion−anion interactions.[40] This is consistent with the X-ray structural data on **1** and **2**, which indicate that the **1**Na units in **1** associate in a dimerlike fashion whereas in **2** the clusters are well isolated in the lattice containing sodium and water. The additional bands at 1055, 540, and 460 cm^{-1} are attributable to $[Cu(en)_2(H_2O)_2]^{2+}$ based on comparison with a sample of $Cu(en)_2(NO_3)_2$. The diffuse-reflectance UV−vis spectrum of **1** is shown in Figure 2B. There is a λ_{max} at 383 nm for the Cu^{II} d−d transition that is red-shifted 26 nm from that of $Cu(en)_2(NO_3)_2$ (λ_{max} at 357 nm) because of the weakening of the ligand field by the polyanion.[42–44] The difference in the reflectance intensity of **1** and $Cu(en)_2(NO_3)_2$ is partially attributed to the mass percent of copper present in the compounds (4.7% vs 21%, respectively).[44]

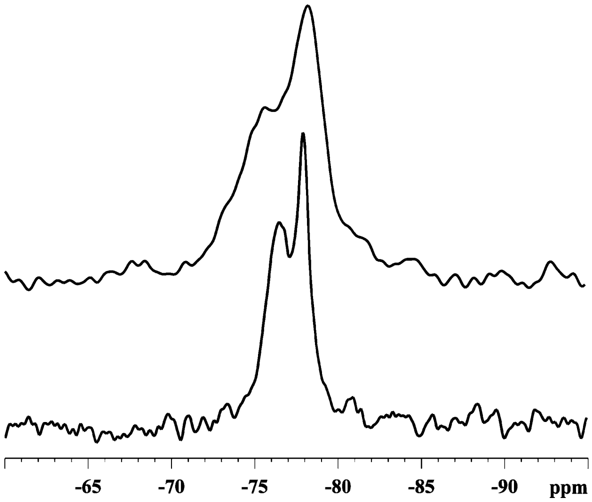

Figure 3. ^{29}Si MAS NMR of **1** (top) and **2** (bottom).

The ^{29}Si MAS NMR spectra of **1** and **2** are shown in Figure 3. In a previous work, **2** was shown to have two peaks at −77.9 ppm (86 Hz) and −76.4 ppm (156 Hz) for the two pairs of symmetry-equivalent internal $[SiO_4]^{4-}$ and external $[SiO_3(OH)]^{3-}$ tetrahedra, respectively.[24] The latter assignment was based on ^1H−^{29}Si cross-polarization (CP) MAS NMR (single peak at −76.4 ppm), suggesting that the external SiO_4

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tetrahedra have a hydroxyl ligand and/or are in close proximity to water. In complex **1**, two close overlapping resonances are observed at −78.2 ppm (151 Hz) and −75.5 ppm (257 Hz). Deconvolution indicates that the ratio of the peaks is ~1:1. The peak widths in **1** are approximately 70% larger than those in **2** because of the close proximity of $[Cu(en)_2(H_2O)_2]^{2+}$. In addition, no CP signal was observed for **1**, most likely because of the fast relaxation of the ^1H spins by copper. However, the assignment of the two peaks at −78.2 and −75.5 ppm to the two pairs of internal $[SiO_4]^{4-}$ and external $[SiO_3(OH)]^{3-}$ tetrahedra in **1** is based on the structural similarities of the $[Na(SiOH)_2Si_2Nb_{16}O_{54}]^{13-}$ units in **1** and **2**.

Discussion

The structure of **1** bears a striking resemblance to the classic sandwich-type polyoxometalates formed by the fusion of two tritungsten-vacant Keggin or Wells-Dawson synthons with one or more d-electron metals and usually charge-balanced with alkali cations.[32] However, in **1**, the roles of sodium and copper are reversed because it is sodium that joins the two **1**Na units together. Four of the six linking sodium atoms in **1** form very strong bonds to the **1**Na units (Na−O, 2.3−2.4 Å), but the stability of **1** could not be assessed in solution by ^{23}Na or ^{29}Si NMR because of its low solubility in water (~2 mM) and organic solvents. Previous studies on $[Nb_6O_{19}]^{8-}$ suggest that the K^+ salt is considerably more soluble in water than the Na^+ salt.[9,10,29] Therefore, we attempted to recrystallize **1** as a K^+ salt, but the addition of KCl to a 2 mM solution of **1** rapidly precipitates **1** with no incorporation of K^+ based on scanning electron microscopy/energy-dispersive spectrometry and FT-IR. We also attempted to assess the pH stability range of **1** in water because the mixed solvent system used to prepare **1** renders the pH ill-defined during synthesis. The pH of a 1.5 mM solution of **1** in pure water is ~9.2, and the compound was stable with the addition of 0.5 M HCl to pH 8.7. At pH <8.7, a lavender precipitate forms with an infrared spectrum similar to that of **2**.[45] The precipitate can be redissolved at room temperature by the addition of 0.5 M KOH to pH 9.2. The slow evaporation of this solution resulted in the formation of microcrystals that were assessed by single-crystal X-ray diffraction.[46] The incorporation of a single potassium resulted in a one-dimensional chain material (Figure 4) with the formula $[Cu(en)_2]_{1.5}[Cu(NH_3)_4]_{0.5}[NH_3CH_2CH_2NH_3]_2KNa_3$-$[Na(SiOH)_2Si_2Nb_{16}HO_{54}]\cdot 18H_2O$ (**3**). The linking potassium has eight K−O bonds (2.8−3.0 Å). There are five bonds to the two adjacent **1**Na clusters and three bonds to water. Despite the excess of potassium in the solution, sodium is still present in the pocket of the cluster, illustrating that this lacunary pocket is ideal for Na^+ coordination (four $Na-O_{cluster}$ bonds at ~2.4 Å). The potassium bonds to the two **1**Na clusters rather asymmetrically so that it shares an edge with the pocket sodium of one cluster and is bonded to the "closed" side of the second cluster (see Figure 4).

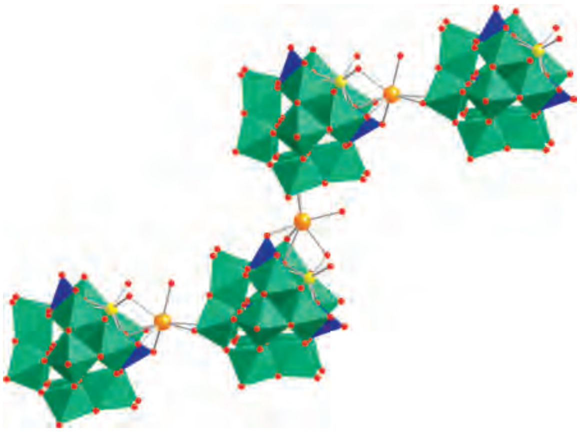

Figure 4. Combination ball-and-stick/polyhedral representation of the K^+-linked $[Na(SiOH)_2Si_2Nb_{16}HO_{54}]^{12-}$ units present in **3**. The NbO_6 octahedra are shown in green, the $SiO_4/SiO_3(OH)$ tetrahedra are shown in blue, and the K, O, and Na atoms are shown in orange, red, and yellow, respectively. One of the water molecules around the potassium has been omitted for clarity.

Conclusions

The prolonged heating of hydrated **2** and $Cu(NO_3)_2$ in a mixed water−en solvent yields the pseudosandwich-type complex **1**. The structure consists of two **1**Na units linked by six sodium atoms, and each pseudosandwich-type complex is charge-balanced by five $[Cu(en)_2(H_2O)_2]^{2+}$ complexes and three additional sodium atoms. Unlike sandwich-type heteropolytungstates, the **1**Na units are linked exclusively by sodium instead of one or more d-electron metals. The results presented here suggest that the alkali cations are playing a prominent role in the synthesis of **1**. The close association observed between the alkali metals and all heteropolyniobates structurally characterized to date indicates that strong ion pairing directs much of their aqueous phase behavior,[24–30] and it is consistent with previous reports that pairing of alkali metals can influence the formation of heteropolytungstates as well.[47] The next challenge for polyoxoniobate chemistry is the selection of appropriate mixed solvent systems that will sufficiently perturb the interactions between the alkali metals and the heteropolyniobates, as well as facilitate the incorporation of d-electron metals, so that new structures and cluster compositions may be discovered.

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(45) The infrared spectrum of the lavender precipitate (from 1100−525 cm^{-1}) has bands at 1002 (w), 976 (w), 922 (w), 854 (s), 771 (m), 718 (w), 654 (s), and 542 (s).

(46) The crystals of **3** were too small for conventional single-crystal X-ray diffraction, so the data were collected on a 15-ID ChemMatCARS beamline equipped with a Bruker 6000 CCD detector at Advanced Photon Source, Argonne National Laboratory. The data were collected at 100 K with a wavelength of 0.49594 Å, an exposure time of 1 s/frame, and a detector distance of 5.0 cm. Data were collected down to a resolution of 0.5527 $Å^{-1}$. The crystals were of poor quality, so details of the disordered solvent molecules and sodium ions could only be determined semiquantitatively. However, the structure of the cluster itself was still well determined, and the results indicate that the compound is a one-dimensional zigzag chain of $[Na(SiOH)_2Si_2Nb_{16}HO_{54}]^{12-}$ units connected by K^+.

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Supporting Information Available: Crystal data for **1** (in CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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