The First Organically Templated Open-Framework Niobium Silicate and Germanate Phases: Low-Temperature Hydrothermal Syntheses of $[(C_4N_2H_{11})Nb_3SiO_{10}]$ (NSH-1) and $[(C_4N_2H_{11})Nb_3GeO_{10}]$ (NGH-1)**

Robin J. Francis* and Allan J. Jacobson

Stable, crystalline, microporous materials are of immense practical importance for commercial applications such as catalysis, absorption, ion-exchange, and separation.[1, 2] The continuing need for microporous materials that display new framework topologies and novel catalytic properties has spurred increasing interest in extending the range of known structure types and compositions. To date, the vast majority of microporous materials are constructed from tetrahedral building units.[3, 4] A much smaller class of materials are those constructed from mixed octahedral–tetrahedral frameworks. Such materials are likely to display framework topologies and properties that are substantially different from those observed in purely tetrahedral materials.[5] However, a limited number of such mixed frameworks have been reported to date.

The synthesis of microporous niobium silicates and germanates is a particularly unexplored area. The only structurally characterized examples are niobium-containing nenadkevichite analogues,[6] and an open-framework potassium niobium germanate, $[K_3Nb_5GeO_{16}]\cdot 2H_2O$, synthesized hydrothermally at very high temperatures and pressures.[7] The hydrothermal synthesis of a microporous sodium niobium silicate, AM-11, has been reported, but its structure is currently unknown.[8] We are not aware of any reported syntheses of organically templated niobium silicate or germanate materials performed under mild ($<200\,^{\circ}C$, $P<25$ atm) hydrothermal conditions.

We report here the synthesis of the first organically templated open-framework niobium silicate and germanate phases, namely $[(C_4N_2H_{11})Nb_3SiO_{10}]$ (NSH-1) and $[(C_4N_2H_{11})Nb_3GeO_{10}]$ (NGH-1).

$[(C_4N_2H_{11})Nb_3SiO_{10}]$ (NSH-1) and $[(C_4N_2H_{11})Nb_3GeO_{10}]$ (NGH-1) were synthesized in high yield (> 70 % based on Nb) under hydrothermal conditions. The structures of NSH-1 and NGH-1 were solved from powder diffraction data, and refined by using the Rietveld method.[9] NSH-1 and NGH-1 are isostructural. The framework asymmetric unit of NSH-1 is shown in Figure 1 a. The open-framework structure of NSH-1 and NGH-1 can be viewed as being formed from two interconnected chainlike structural motifs. The first consists of two edge-shared $Nb(2)O_6$ octahedra that are further connected by corner-shared O(6) atoms to form infinite double columns running along the [010] direction. A second chain of $[NbO_6\text{-}Si(Ge)O_4\text{-}NbO_6]_n$ polyhedra is formed from corner-sharing $Nb(1)O_6$ octahedra and $Si(Ge)O_4$ tetrahedra and runs along the [100] direction. The two chains are cross-linked through O(4) atoms to form the open-framework structure.

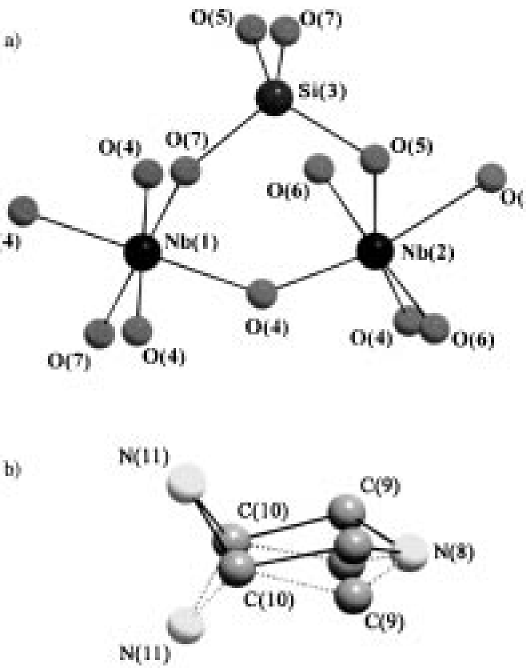

Figure 1. a) The framework asymmetric unit of $[(C_4N_2H_{11})Nb_3SiO_{10}]$ (NSH-1) showing the local coordination and the atomic-labeling scheme. b) The two possible orientations of the piperazine template due to statistical disorder of the C(9) and N(11) atoms.

The Nb(1) atoms reside at the center of an almost regular octahedron with an average Nb–O distance of 2.050(7) Å for NSH-1 and 1.977(8) Å for NGH-1. The Nb(2) atom resides in a somewhat more distorted coordination with a d_{av}(Nb–O) of 2.011(6) Å for NSH-1 and 2.032(9) Å for NGH-1. The Si or Ge atoms reside at the center of an almost perfectly regular tetrahedron with a d_{av}(Si–O) of 1.6156(5) Å for NSH-1 and a d_{av}(Ge–O) of 1.775(13) Å for NGH-1. The results of bond valence sum calculations[10] for the Nb, Si, and Ge atoms were in good agreement with the expected values.

The three-dimensional framework structure of NSH-1 and NGH-1 (shown in Figure 2) consists of a network of three interconnecting one-dimensional channels, two consisting of six-membered rings (6-MR) of polyhedra and the other an eight-membered ring (8-MR). The two 6-MR channels are formed from six NbO_6 corner-linked units. The first runs along the [100] direction; the second along the [111] direction. The 8-MR channels are constructed from six NbO_6 and two GeO_4 units and run along the [010] direction perpendicular to one of the 6-MR channels and at an angle of 55° to the other. The

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[*] Dr. R. J. Francis, Prof. A. J. Jacobson
Department of Chemistry
University of Houston
Houston, TX 77204-5641 (USA)
Fax: (+1) 713-743-2787
E-mail: robin@xray.phys.uh.edu

[**] We thank the National Science Foundation (DMR-9805881) and the Robert A. Welch Foundation for support. This work made use of MRSEC/TCSUH Shared Experimental Facilities supported by the National Science Foundation under Award Number DMR-9632667 and the Texas Center for Superconductivity at the University of Houston. Work at the National Synchrotron Light Source at Brookhaven National Laboratory was partially supported by the Division of Materials Sciences, U.S. Departmentof Energy under contract DE-AC02-98CH10886. We thank Dr. Kent Ross for collecting the energy-dispersive X-ray analysis (EDAX) data and scanning electron microscopy (SEM) data, and Dr. Tom Vogt for assistance in collecting the X7A powder data.

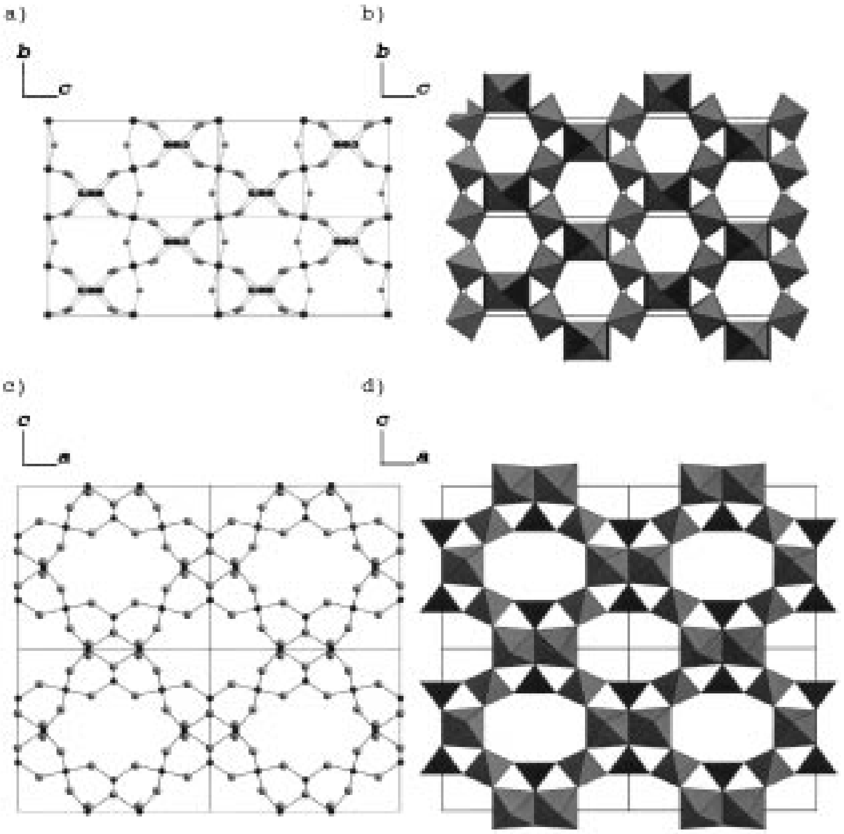

Figure 2. a, b) Representations of the framework structure of $[(C_4N_2H_{11})Nb_3SiO_{10}]$ (NSH-1) and $[(C_4N_2H_{11})Nb_3GeO_{10}]$ (NGH-1) viewed along the *a* axis, showing the 6-MR channels. c, d) Representations of the framework viewed along the *b* axis, showing the larger 8-MR channels. The niobium, silicon (germanium), and oxygen atoms atoms are represented as black, medium gray, and light gray spheres, respectively. In b) and d) NbO_6 octahedra are shown in gray, $Si(Ge)O_4$ tetrahedra in black. The template molecules are omitted for clarity.

three channels intersect at approximately (0, 0.25, 0.125) forming an irregular, roughly triangular shaped cavity centered at that position (see Figure 3). The 6-MR channels are almost circular in cross-section with a shortest oxygen–oxygen distance across the channel of 5.6 Å, giving a "free-pore diameter" (using the atomic radii of Shannon[11]) of about 2.8 Å. The large 8-MR channels are elliptical in shape with an approximate free-pore diameter of 3.4 × 5.0 Å. The maximum free-diameter across the cavity is approximately 5.7 Å. The piperazinium cations reside in the center of the cavities. One of each of the two carbon and nitrogen atoms are statistically disordered over two sites giving rise to two possible orientations of the piperazinium cations as shown in Figure 1b. On the basis of charge-balance considerations the piperazine molecules are assumed to be monoprotonated. This is consistent with the pH value of the reaction (ca. 9) and the pK_a values for piperazine in aqueous solution.[12] Very strong hydrogen bonds are observed between the N(8) atom, two O(5) atoms, and two O(6) atoms (N−O distances 2.7–2.9 Å). Somewhat weaker hydrogen bonds are formed between the N(11) atoms and two O(7) atoms (N−O distance 3.1 Å). As can be seen from Figure 3 the piperazinium cation is a very good "fit" for the cavity of NSH-1 and NGH-1.

The structure of NSH-1 and NGH-1 shows some similarities to the structure of $[K_3Nb_5GeO_{16}]\cdot 2H_2O$. In particular infinite double columns of NbO_6 octahedra and $[NbO_6\text{-}Si(Ge)O_4\text{-}NbO_6]_n$ chain motifs are observed in both structure types. However, in $[K_3Nb_5GeO_{16}]\cdot 2H_2O$ single vertex-sharing columns of NbO_6 octahedra are found, whereas NSH-1 and NGH-1 contain only double columns. As a result while in NSH-1 and NGH-1 cavities are only formed at the intersection of the larger 8-MR channels and the 6-MR channels, in $[K_3Nb_5GeO_{16}]\cdot 2H_2O$ smaller cavities are also formed at the intersection of two 6-MR channels. The structural differences are undoubtedly caused by the difference in sizes of the K^+ and piperazinium cations.

Elemental analyses of NSH-1 and NGH-1 consistently gave a Nb:Si/Ge ratio of less than the 3:1 suggested by the X-ray diffraction data. Niobium vacancies within the structures of NSH-1 and NGH-1, either distributed statistically throughout the structure or present as extended layer-like defects, are the most likely cause of the difference from the ideal stoichiometry. Close inspection of the powder diffraction patterns reveals that the widths of each of the reflections are not exactly equal. In particular, the 101 reflection is significantly broadened relative to the 011 reflection, indicating disorder in the [101] lattice direction. Inspection of the structure suggests a

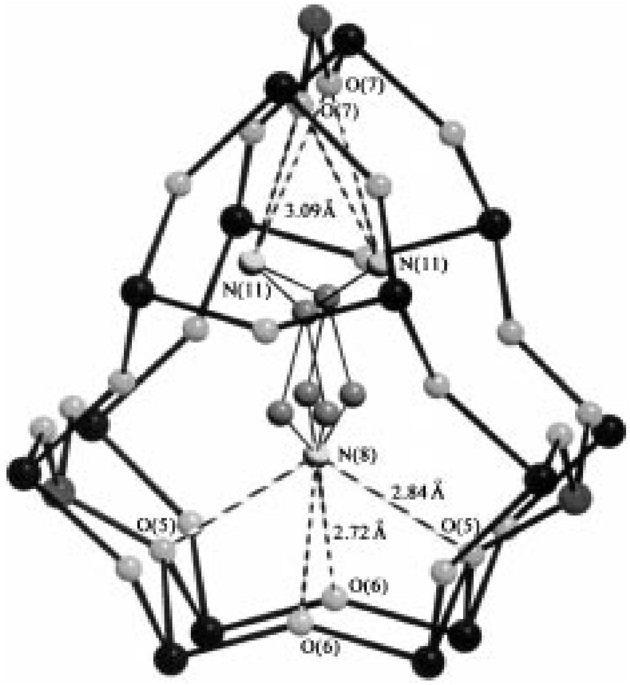

Figure 3. The location of the piperazinium cations in the cavities formed at the intersection of the 6-MR and 8-MR channels. The niobium, silicon (germanium), and oxygen atoms atoms are represented as black, medium gray, and light gray spheres, respectively. The two possible orientations of the template are shown. Hydrogen bonding interactions are shown by dashed lines.

mechanism by which disorder can be introduced in this direction that also accounts for the observed niobium deficiency. If all of the Nb(1) atoms in a (101) "layer" are removed, the remaining structural motifs can be connected through corner-shared Nb(2) and Si(Ge) polyhedra to form structures containing six-membered channels along the [010] direction. Modeling studies suggest that if such layers of Nb(1) atoms are removed at random, order is lost along the [101] direction but maintained in the [011] direction.

Thermal analysis of NSH-1 and NGH-1 revealed that loss of the template occurs between about 200 and 520 °C. Powder X-ray diffraction patterns of samples of NSH-1 and NGH-1 heated for 1–2 h at 350 and 440 °C, respectively, indicated that the frameworks remain intact following loss of the template, although a substantial loss of crystallinity was evident. IR spectroscopy confirmed complete loss of the template from the calcined materials. Heating at substantially higher temperatures produced amorphous materials.

Ion-exchange experiments revealed that the piperazinium cations in NSH-1 and NGH-1 could be successfully exchanged for Na^+ and K^+ ions, as demonstrated by small changes in the powder X-ray diffraction patterns and the diminution in the intensity of the carbon–carbon and carbon–nitrogen stretches in the IR spectra. The materials largely retained their crystallinity following the exchange procedure, although some line broadening was observed.

In summary, we have described the low-temperature hydrothermal synthesis and structure of the first examples of organically templated open-framework niobium silicates and germanates. The materials display thermal stability and ion-exchange capability. Given the large variety of organic templates that could be used in this synthetic regime, and the range of compositions seen in condensed niobium silicates and germanates, the scope for the synthesis of further novel materials in this class appears to be very large.

Experimental Section

Syntheses were conducted hydrothermally in a Teflon-lined autoclave (23 mL).

NSH-1: Nb_2O_5 (0.089 g,99.5 %, Aldrich) was dissolved in aqueous HF (0.167 g 48 wt %, Aldrich) and heated to 110 °C for 4 h. After cooling, this solution was combined with SiO_2 (0.120 g, fumed, 99.8 %, Aldrich), piperazine (0.459 g, 99 %, Aldrich), H_2O (2.88 g), and ethylene glycol (5 g) and heated at 160 °C for 25 days. A fine white powder (particle size ca. 0.2 μm) of NSH-1 was recovered. NGH-1 was synthesized following the same procedure, by using 0.209 g of GeO_2 (99.99 %, Aldrich) instead of the SiO_2. A fine white powder of NGH-1 (ca. 0.4 μm) was obtained after heating at 160 °C for six days.

Ion-exchange reactions were performed by stirring 100 mg samples in 2 M aqueous solutions (10 mL) of either NaCl or KCl at 60 °C for 12 h. Thermogravimetric analyses were performed in flowing dry air on a Thermal Instruments TGA 2950 instrument at a ramp rate of 5 K min^{-1}. IR spectra were collected on a Mattson FTIR 5000 spectrometer (KBr method).

Received: March 12, 2001 [Z 16758]

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[9] Powder diffraction data on NGH-1 were collected on beamline X7A of the NSLS, Brookhaven National Laboratory, $\lambda = 0.70117$ Å, over the range 2–47° 2θ. The pattern was indexed by using the orthorhombic cell $a = 13.0861(2)$, $b = 7.4937(2)$, $c = 11.4967(4)$ Å, space group *Imma* (no. 74). The structure was solved by using the direct methods package EXPO.[13] This solution was then used in the Rietveld analysis of the structure using the software package GSAS.[14] The template atom positions were determined from difference Fourier syntheses. Soft constraints were applied to the C–C and C–N bond lengths in the refinement. The final refinement consisted of 70 structural and profile parameters and proceeded smoothly to convergence, with $R_p = 0.0605$, $R_{wp} = 0.0716$, $R_F = 0.0552$, $R_F2 = 0.0778$, $\chi^2 = 7.732$. Powder diffraction data on NSH-1 were collected on a Scintag 2000 diffractometer using Cu radiation over the range 8–100° 2θ. Unit cell refinement gave $a = 12.9041(4)$, $b = 7.4967(3)$, $c = 11.4471(5)$ Å, space group *Imma*. The structure solution of NGH-1 was used as the starting model in the Rietveld analysis. The refinement proceeded smoothly to convergence, with $R_p = 0.0590$, $R_{wp} = 0.0459$, $R_F = 0.0609$, $R_F2 = 0.0722$, $\chi^2 = 0.9493$. Soft constraints were applied to the C–C and C–N bond lengths. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no." CCDC-163346 (NSH-1) and CCDC-163347 (NGH-1). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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A Lewis Acid Catalyst Anchored on Silica Grafted with Quaternary Alkylammonium Chloride Moieties**

Thundi M. Jyothi, Mark L. Kaliya, and
Miron V. Landau*

The development of novel catalytic materials based on mesoporous supports by chemically binding the active species on their surfaces has become of profound importance in recent years owing to the benefits of catalyst heterogeniza-

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[*] Prof. M. V. Landau, Dr. T. M. Jyothi, Dr. M. L. Kaliya
Blechner Center for Industrial Catalysis and Process Development
Department of Chemical Engineering
Ben Gurion University of the Negev
Beer Sheva-84105 (Israel)
Fax: (+972) 8-6472902
E-mail: mlandau@bgumail.bgu.ac.il

[**] T.M.J. is grateful to the Blechner fund for a postdoctoral fellowship.