A General Synthetic Procedure for Heteropolyniobates

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The heteropolyanions of W, Mo, and V, which have found numerous applications, are formed simply by acidification of solutions of their oxoanions. Under similar conditions, these oxoanion precursors are not available for Nb, and Nb-oxo chemistry is dominated by formation of the Lindquist ion $[Nb_6O_{19}]^{8-}$ only. However, heteropolyniobate formation is favored in hydrothermal reactions of aqueous, alkaline precursor mixtures. Here we give two examples of heteropolyniobates formed by this general reaction type: $K_{12}[Ti_2O_2][SiNb_{12}O_{40}]\cdot 16H_2O$ [1], which contains chains of silicododecaniobate Keggin ions, and $Na_{14}[H_2Si_4Nb_{16}O_{56}]\cdot 45.5H_2O$ [2], a new heteropolyanion structure type.

Polyoxometalates (POMs) comprise a versatile class of inorganic, anionic clusters that has made a mark on disciplines as diverse as medicine (*1*), catalysis (*2*), materials science (*3*), geochemistry (*4*), nuclear waste processing (*5*), and applications involving photochemical or electrochemical response (*6*). POMs can be further subcategorized as isopolyanions and heteropolyanions (*7*). An isopolyanion consists exclusively of an assembly of edge- and corner-sharing octahedra of d^0 early transition metals, whereas the heteropolyanions contain one or more central tetrahedra, about which these octahedra are assembled (*8*). Heteropolyanion chemistry is dominated by heteropolytungstates, -molybdates, and -vanadates and are usually obtained by precipitation from aqueous, acidified solutions at ambient temperature and pressure. Furthermore, isopolyanion chemistry is dominated by W, Mo, and V anionic clusters obtained from acidified solutions.

Isopolyanions of Ta and Nb can also be obtained from basic solutions. Isopolyniobate chemistry is dominated by the $[Nb_6O_{19}]^{8-}$ Lindquist ion (*5*, *9*–*12*), and the formation and structural characterization of $[Nb_{10}O_{28}]^{6-}$ (*13*) has been reported once. The isopolytantalate Lindquist ion, $[Ta_6O_{19}]^{8-}$ (*14*) is known as well. However, heteropolyniobate and heteropolytantalate chemistry remain relatively unexplored compared with their close periodic neighbors W, Mo, and V, which exhibit diverse heteropolyanion assemblies (*7*). We introduce a general synthetic procedure that favors the formation of heteropolyniobates and report two examples of heteropolyniobates: one featuring chains of silicododecaniobate Keggin ions [1] and a second containing isolated, oval shaped clusters centered about a Si_2O_7 dimer [2].

Our synthetic method relies on hydrothermal treatment of mixtures of amorphous metal oxides and/or metal alkoxides in basic, aqueous solutions (*15*). Our synthetic route to heteropolyniobates differs from those used to produce heteropolyvanadates, -molybdates, and -tungstates in (i) solubility of precursors, (ii) conditions required for precursor solubilization, and (iii) existence of stable competing phases. Vanadium, tungsten, and molybdenum form the very soluble and easily manipulated oxoanions, such as MoO_4^{2-}, WO_4^{2-}, VO_4^{2-}, and VO_4^{3-}. Acidification of solutions of these oxoanions in the presence of the central tetrahedral cation and countercations leads to the formation of heteropolyanions, often precipitated at room temperature (*7*). No such easily dissolvable oxoanions are available for Nb, and most synthetic procedures for isopolyniobates report using freshly precipitated, hydrated Nb_2O_5, or a fusion of an alkali carbonate or hydroxide with Nb_2O_5 (*7*).

To dissolve these Nb precursors using the same "beaker chemistry" that is used for the polyoxovanadates, -tungstates, and -molybdates (e.g., in water at 20° to 100°C and ambient pressures in a non-inert atmosphere), many excess equivalents of base are required. However, as the concentration of AOH (where A represents alkali) increases in solution, the Lindquist $A^+_8[Nb_6O_{19}]^{8-}$ compound is salted out as a major product. Spectroscopic studies have shown that the Lindquist ion is indeed the dominant species of Nb in solutions of pH > 7 at ambient conditions (*7*, *16*). Therefore, forming other polyoxoniobate clusters requires finding conditions in which the Nb precursor will dissolve but the Lindquist $[Nb_6O_{19}]^{8-}$ ion is not the dominant species.

By carrying out the reactions in an autoclave, we found that increased temperatures (170° to 250°C) and autogenous pressures of water made possible the dissolution of the Nb precursors and precipitation of heteropolyniobates without the huge excess of base that favors $[Nb_6O_{19}]^{8-}$ precipitation. To form [1] and [2], AOH:Nb (where A = Na, K) ratios are closer to stoichiometric (2.5:1 and 1.5:1, respectively), compared with ~10:1 for dissolution of the Nb precursor and precipitation of the $[Nb_6O_{19}]^{8-}$ ion using the standard "beaker chemistry." We attempted to replicate the synthesis for the formation of [2] without the hydrothermal treatment. As expected, dissolution of the precursor mixture never occurred, even when the water was boiled. A competing phase to the formation of polyoxoniobates in hydrothermal aqueous reactions involving Nb and an alkali hydroxide is very stable perovskite, $LiNbO_3$, $NaNbO_3$, or $KNbO_3$. However, perovskite formation can be avoided by using short reaction times (i.e., 24 hours or less).

The phase containing the silicododecaniobate Keggin ion, $K_{12}[Ti_2O_2][SiNb_{12}O_{40}]\cdot 16H_2O$ [1], grows as needle-like, colorless crystals (*17*) suitable for single-crystal x-ray diffraction. The silicododecaniobate cluster exhibits the typical α-Keggin ion geometry of a tetrahedral arrangement of four triads of edge-sharing NbO_6 octahedra, with the triply bridged oxygen of each triad bonded to the central tetrahedral silicon (*18*). The Keggin ions are then linked along the *c* direction by a dimer of edge-sharing, distorted TiO_6 octahedra, giving rise to infinite Keggin ion chains. The two alternating building blocks of the chains are best described as $[Ti_2O_2]^{4+}$ and $[SiNb_{12}O_{40}]^{16-}$, and are illustrated in (Fig. 1A). This linkage is the same type described by Müller *et al.* (*19*) for a phase that features mixed Mo-V Keggin ions linked by V_2O_2 bridges. Each octahedrally coordinated Ti atom is bound to four of the Keggin O atoms that frame a four-ring "window," and the two remaining O atoms are shared between two Ti atoms. Therefore, each TiO_6 octahedron shares edges with four NbO_6 octahedra within the Keggin cluster and one TiO_6 octahedron that is linked to the next Keggin cluster. This constrained geometry gives rise to extreme angular distortion of the TiO_6 octahedron (O-Ti-O bond angles range from ~77° to 113°). The infinite anionic chains are not linked within the *ab* plane, and the charge-balancing cations (K^+) and water molecules are located between the chains (Fig. 1B). ^{29}Si solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy of [1] gives a single peak

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at –75.9 ppm, corresponding with the single crystallographic Si site.

The second heteropolyniobate phase, $Na_{14}[H_2Si_4Nb_{16}O_{56}]\cdot 45.5H_2O$ [2], grows as large, colorless crystals suitable for single-crystal x-ray analysis (*17*). It contains isolated clusters that are separated by the charge-balancing sodium cations along with H_2O molecules. The geometrical arrangement of the NbO_6 octahedra of the $[H_2Si_4Nb_{16}O_{56}]^{14-}$ cluster may be described as a fusion of two partial (3/4) Keggin ions. Each partial Keggin ion consists of three triads of edge-sharing octahedra (nine NbO_6 octahedra) wrapped around a SiO_4 tetrahedra, with the fourth capping triad removed. Two NbO_6 octahedra of the 3/4 Keggin ions are common to the two halves of the cluster. It is through these common octahedra that the 3/4 Keggin subunits are "fused," giving a total of 16 NbO_6 octahedra. This fusion gives rise to two sets of five edge-sharing octahedra in an "Olympic ring" arrangement. Those two sets are then linked together by corner-sharing of their linear triad of octahedra. The cluster is shown in Fig. 2 in three different colors to emphasize the relation between this structure and the α-Keggin structure. The NbO_6 octahedra of the two 3/4 Keggin subunits are red and blue, respectively. The two NbO_6 octahedra common to both subunits are purple.

The removal of the third capping triad of the partial Keggin subunits leaves the central Si with only three O bonds. Corner-sharing with the Si of the second subunit forms the fourth Si-O bond, which gives rise to a heteropolyanion centered about an Si_2O_7 (Si1 and Si2) dimer. In most heteropolyanion structures containing two central polyhedra, such as the Dawson geometry (*8*, *20*), the central tetrahedra are not linked together. However, several structures centered about a P_2O_7 dimer have been reported (*21*, *22*).

Diametrically opposed to the two NbO_6 octahedra common to the partial Keggin subunits (Fig. 2) are two surface SiO_4 (Si3 and Si4) tetrahedra. They form a six-ring window along with four NbO_6 octahedra. Three corners of these surface SiO_4 tetrahedra are bonded within the cluster, and the fourth Si-O bond is terminal. However, unlike the typical polyoxometalate surface polyhedra that have a very short exterior M-O bond, the $Si\text{-}O_{terminal}$ bond is the longest of the four Si-O bonds for both of the surface SiO_4 (Si3 and Si4) tetrahedra. The $Si4\text{-}O27_{terminal}$ bond length is 1.65 Å and the $Si3\text{-}O24_{terminal}$ bond is 1.68 Å, where the average Si-O bond length for both these surface SiO_4 tetrahedra is 1.63 Å. To determine whether O24 and O27 are actually OH^- groups, we used bond valence sum (BVS) calculations (*23*) and $^1H\text{-}^{29}Si$ cross polarization (CP) MAS NMR spectroscopy. The BVS calculations revealed that the valencies of all metal and oxygen atoms within the cluster were satisfied by their intracluster bonds, with the exception of O24 and O27 that had a BVS less than 1 (expected, ~2). This result suggests that O24 and O27 are indeed OH^- groups. The extra-cluster species (Na and H_2O) in close proximity to O24 and O27 provide an environment that can accommodate those OH^- groups. Direct solid-state ^{29}Si MAS NMR of [2] gave two broad peaks at –77.9 ppm and –76.9 ppm, consistent with one resonance for the central Si_2O_7 (Si1 and Si2) and one resonance for the surface SiO_4 (Si3 and Si4). However, the $^1H\text{-}^{29}Si$ CP MAS NMR gave a single peak at –76.9 ppm, corresponding to the surface SiO_4, either in close proximity to water or possessing a hydroxyl ligand. The CP behavior as a function of contact time, with a maximum at ~750 μs, was consistent with Si-OH species. Finally, the width of the peak obtained by the CP experiment sug-

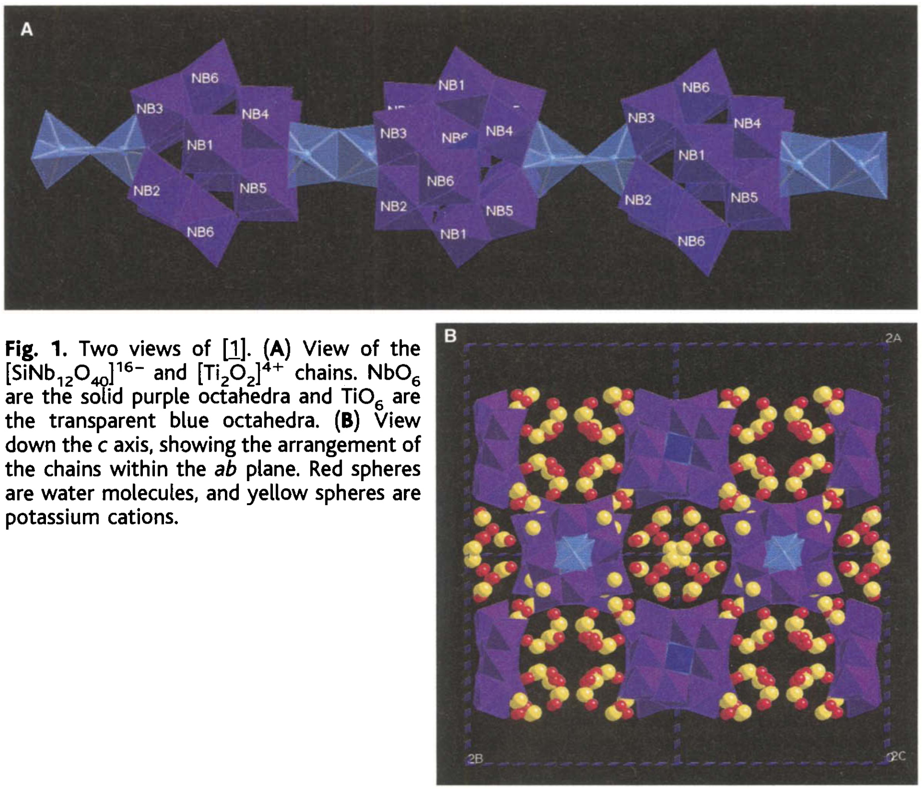

Fig. 1. Two views of [1]. (**A**) View of the $[SiNb_{12}O_{40}]^{16-}$ and $[Ti_2O_2]^{4+}$ chains. NbO_6 are the solid purple octahedra and TiO_6 are the transparent blue octahedra. (**B**) View down the *c* axis, showing the arrangement of the chains within the *ab* plane. Red spheres are water molecules, and yellow spheres are potassium cations.

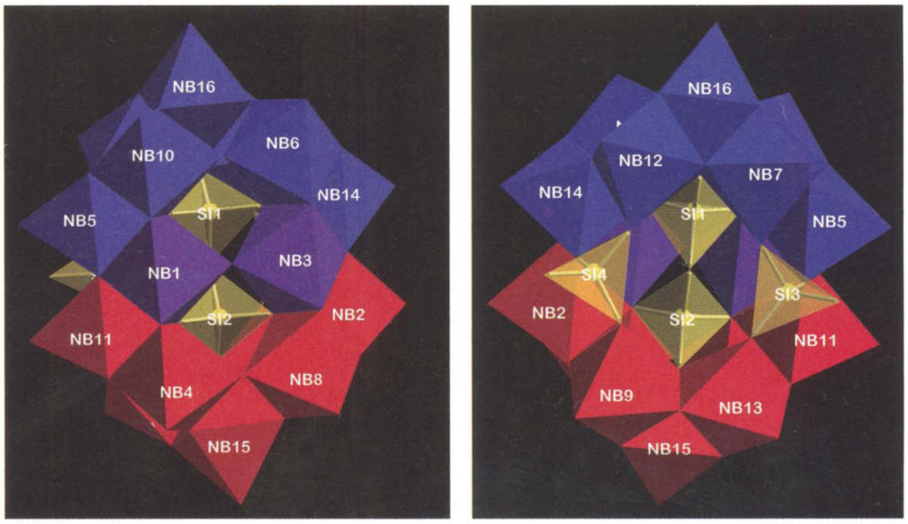

Fig. 2. Two views of the $[H_2Si_4Nb_{16}O_{56}]^{14-}$ cluster of [2], color-coded to show the relation between this cluster and the α-Keggin structure. The blue NbO_6 octahedra compose one 3/4-Keggin subunit, the red NbO_6 octahedra compose the second 3/4-Keggin subunit, and the two purple NbO_6 octahedra are shared between the two "fused" subunits. SiO_4 tetrahedra are transparent yellow.

gested more than one Si-OH specie, which is in accordance with the unresolved overlap of Si3 and Si4 bonded to terminal OH^- groups.

Although the $[H_2Si_4Nb_{16}O_{56}]^{14-}$ cluster of [2] is insoluble in the aqueous NaOH solution (pH ~ 13.5) from which it precipitates, it is easily dissolved intact at room temperature in a less basic solution (pH ~7 to 11 before cluster dissolution). Figure 3 shows solution ^{29}Si NMR of [2] dissolved in pure deionized water. The two peaks at –79.3 and –78.5 ppm correspond with the central Si_2O_7 (Si1 and Si2) and surface SiO_4 (Si3 and Si4), respectively, which confirms that the cluster remains intact upon dissolution. Further, it can be re-precipitated by slow diffusion of methanol into the aqueous solution at room temperature. The re-precipitated crystals were identified as [2] by x-ray diffraction.

We also explored other reputed synthetic routes. Graeber and Morosin (*13*) used a nonaqueous solvent to produce an isodecaniobate at ambient conditions. In this method, niobium alkoxide was dissolved in methanol with NMe_4OH in an approximate stoichiometric NMe_4:Nb ratio of around 0.5:1 to form the $[Nb_{10}O_{28}]^{6-}$ isopolyniobate at ambient temperature and pressure. We carried out the same reaction using NaOH instead of NMe_4OH, which results in a rapid and uncontrolled precipitation of amorphous oxides. We also used Graeber and Morosin's technique with the addition of a silicon alkoxide in attempt to form SiO_4-centered heteropolyniobates, which resulted in the formation of amorphous gels. Though Graeber and Morosin's procedure does allow for dissolution of Nb precursors at ambient conditions, it is limited to reactions using organic counter-cations in order to solubilize the hydrolysis and condensation intermediates of metal alkoxides as well as the polyoxometalate products. In fact, the use of organic counter-cations is a known process to render polyoxometalates soluble in nonpolar solvents (*24*). Further, reactions that involve base hydrolysis and condensation of metal alkoxides in open containers are inherently not reproducible. The reactions that occur and, thus, the products that form are extremely sensitive to (i) the degree of prehydrolysis and condensation of the metal alkoxides and (ii) the amount of water present in the reaction mixture. These conditions are, in turn, dependent on uncontrollable parameters such as the initial metal alkoxide purity, storage conditions, age of the metal alkoxide, the atmospheric humidity on the day(s) the reactions is executed, and the amount of moisture present in hygroscopic starting materials, such as alcohol solvents and alkylammonium hydroxide.

Although niobium alkoxides can also be used in our hydrothermal approach, they undergo rapid and complete hydrolysis and condensation in aqueous solution to form freshly precipitated Nb oxide, even before autoclaving. The hydrothermal treatment that follows results in digestion of the freshly precipitated metal oxides, as evidenced by the high yields, good purity, and reproducible syntheses of both [1] and [2]. Finally, relatively severe conditions like hydrothermal treatment may be required to break up stable $[Nb_6O_{19}]^{8-}$ isopolyanions to obtain the smaller NbO_6-containing units (i.e., monomers, dimers, and trimers) that are the building blocks for heteropolyanions.

The two phases [1] and [2] reported here resulted from the investigation of a narrow range of synthesis parameters. A huge amount of phase space has yet to be covered by a larger effort that includes variations in counterion, tetrahedral metal, heterometals, alkali concentration, metal oxide precursor concentration, and temperature.

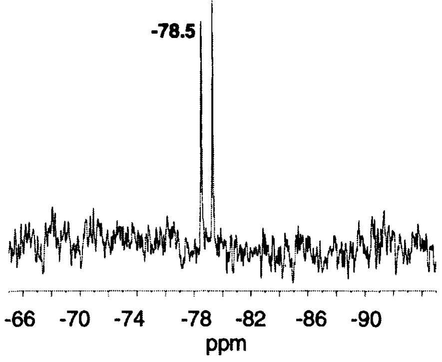

Fig. 3. ^{29}Si NMR spectrum of [2] in solution. The peak at –79.3 ppm is corresponds with the central Si_2O_7 (Si1 and Si2). The peak at –78.5 ppm corresponds with Si3 and Si4, the surface Si atoms.

References and Notes

1. J. T. Rhule, C. L. Hill, D. A. Judd, *Chem. Rev.* **98**, 327 (1998).
2. N. Mizuno, M. Misono, *Chem. Rev.* **98**, 199 (1998).
3. E. Coronado, C. J. Gomez-Garcia, *Chem. Rev.* **98**, 273 (1998).
4. W. H. Casey, B. L. Phillips, *Geochim. Cosmochim. Acta* **65**, 705 (2001).
5. A. V. Besserguenev, M. H. Dickman, M. T. Pope, *Inorg. Chem.* **40**, 2582 (2001).
6. D. E. Katsoulis, *Chem. Rev.* **98**, 359 (1998).
7. M. T. Pope, *Heteropoly and Isopoly Oxometalates* (Springer-Verlag, New York, 1983).
8. Y. P. Jeannin, *Chem. Rev.* **98**, 51 (1998).
9. B. W. Dale, M. T. Pope, *J. Chem. Soc. Chem. Commun.* **67**, 792 (1967).
10. C. M. Flynn, G. A. Stucky, *Inorg. Chem.* **8**, 335 (1969).
11. M. F. P. Silva, A. M. V. Cavaleiro, J. D. P. DeJesus, *J. Coord. Chem.* **50**, 141 (2000).
12. B. W. Dale, J. M. Buckley, M. T. Pope, *J. Chem. Soc. A.* **1969**, 301 (1969).
13. E. J. Graeber, B. Morosin, *Acta Crystallogr.* **B33**, 2137 (1977).
14. H. Hartl, F. Pickhard, F. Emmerling, C. Rohr, *Z. Anorg. Allg. Chem.* **627**, 2630 (2001).
15. Synthesis of $K_{12}[Ti_2O_2][SiNb_{12}O_{40}]16H_2O$ [1] is as follows: 0.364 g KOH (6.5 mmol) was dissolved in 8 ml H_2O (444 mmol). 0.35 g amorphous Nb_2O_5 (2.6 mmol Nb), 0.18 g tetraethylorthosilicate (TEOS, 0.9 mmol), and 0.13 g tetraisopropyltitanium (TIPT, 0.45 mmol) were added and stirred and at room temperature for 30 min. Final mixture ratio of H_2O:K:Nb:Si: Ti = 68:1:0.40:0.14:0.07. The mixture was introduced to a 23 ml autoclave and placed in a 220°C oven for 20 hours. The white crystalline product was collected by filtration and washing with deionized water. Yield = 0.45 g, ~78% based on Nb). Synthesis of $Na_{14}[H_2Si_4Nb_{16}O_{56}]45.5H_2O$ [2] is as follows: 0.96 g NaOH (24 mmol) was dissolved in 50 ml H_2O (2778 mmol). 1.62 g TEOS (7.79 mmol), and 2.1 g amorphous Nb_2O_5 (15.8 mmol Nb) were combined in a 100 ml autoclave and stirred for 30 min. Final mixture ratio was H_2O:Na:Nb:Si = 116:1:0.65:0.32. The mixture was placed in a 220°C oven for 5 to 8 hours. The product was a mixture of predominantly large, colorless crystals and a small amount of a powdery material. The yield was difficult to determine because, upon removal of the mother liquor, the crystals quickly dehydrated. Crystals for x-ray analysis were picked out and rinsed in a NaOH solution (pH 13.5) and quickly covered in oil for storage. To produce pure samples of [2] for further analysis and experiments, the product mixture containing [2] was dissolved in deionized water and filtered to obtain a clear solution. Slow diffusion of methanol into the aqueous solution resulted in the precipitation of well-formed crystals. The yield from recrystallization was ~40 to 50%.
16. G. M. Rozantsev, O. I. Dotsenko, G. V. Taradina, *Russ. J. Coord. Chem.* **26**, 247 (2000).
17. X-ray crystallographic analyses of [1] and [2] were carried out on a Bruker AXS Smart-CCD (Madison, WI) with graphite monochromated Mo-Kα radiation (λ = 0.71069 Å). Crystal data for [1] is as follows: $K_{12}[Ti_2O_2][SiNb_{12}O_{40}]16H_2O$; chemical formula weight, = 2668; tetragonal; space group P-4c2; Z = 4; $T = -105 \pm 2$ °C; a = 15.972 (4) Å, c = 22.956 (6) Å, V = 5856 (2) $Å^3$; goodness of fit = 0.977; R_1 $[I > 2\sigma(I)]$ = 5.75%; wR2 = 14.35% (all data). Crystal data for [2] is as follows: $Na_{14}[H_2Si_4Nb_{16}O_{56}]45.5H_2O$; chemical formula weight = 3639; triclinic; space group P-1; Z = 2; $T = -105 \pm 2$ °C; a = 13.810 (3) Å, *b* = 15.280 (3) Å, *c* = 23.272 (5) Å, α = 75.990 (5)°, β = 81.071 (4)°, γ = 75.072 (4)°, V = 4581 (2) $Å^3$; goodness of fit = 1.053; R_1 $[I > 2\sigma(I)]$ = 7.58 %; wR2 = 20.23 % (all data). For [2], the differentiation between the 14 Na atoms per formula unit required for charge-balance and the water molecules was based on the value of the temperature factor for each site and crystal-chemical considerations. For both [1] and [2], the positions of the hydrogen atoms of the water molecules could not be determined. Full analytical information and crystallographic data can be found in Supporting Online Material on *Science* Online.
18. S. H. Wang, S. A. Jansen, *Chem. Mater.* **6**, 2130 (1994).
19. A. Müller, M. Koop, P. Schiffels, H. Bogge, *J. Chem. Soc. Chem. Commun.* **97**, 1715 (1997).
20. B. Dawson, *Acta Crystallogr.* **6**, 113 (1953).
21. U. Kortz, *Inorg. Chem.* **39**, 623 (2000).
22. ———, M. T. Pope, *Inorg. Chem.* **33**, 5643 (1994).
23. B. E. Brese, M. O'Keefe, *Acta Crystallogr.* **B47**, 192 (1991).
24. D. E. Katsoulis, M. T. Pope, *J. Am. Chem. Soc.* **106**, 2737 (1984).
25. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

Supporting Online Material
www.sciencemag.org/cgi/content/full/297/5583/996/DC1
Full crystallographic information for [1] and [2]

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