A Cavity-Containing Polyoxometalate

DOI: 10.1002/anie.200801883

The $[Ti_{12}Nb_6O_{44}]^{10-}$ Ion—A New Type of Polyoxometalate Structure[**]

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Titanates and niobates are among the most promising materials to catalyze the photolysis of water to yield molecular hydrogen and oxygen.[1] Solid-phase titanoniobate species, such as $MTiNbO_5$ (M = H, Li, K), have been attracting significant interest, but to our knowledge only one discrete homoleptic polyoxotitanoniobate cluster has so far been described, the cluster $Na_8[Ti_2Nb_8O_{28}]$.[2] Herein we describe a second discrete homoleptic polyoxotitanoniobate cluster and a whole new class of polyoxometalates[11] (POMs). This titanoniobate anion, $[Ti_{12}Nb_6O_{44}]^{10-}$, is about 1.5 nm in size, is stable in water at near-neutral pH, and, most interestingly, has a central cavity. It is most similar to, but much larger than, the Lindqvist ions[3] and the central cavity is unique.

During attempts to synthesize $[N(CH_3)_4]_8[Ti_2Nb_8O_{28}]$, we obtained varying amounts of $[N(CH_3)_4]_7[TiNb_9O_{28}]$ as well, based on electrospray ionisation mass spectrometry (ESI-MS). Along with this new compound, we also identified a new type of titanoniobate, $[N(CH_3)_4]_{10}[Ti_{12}Nb_6O_{44}]$ (**1**, Figure 1) The orthogonal crystals of **1** were twinned, and exhibited dichroism under a polarizing microscope, making them easy to isolate. The crystals are readily soluble in water, and ESI-MS investigations of the stability of **1** show that it does not dissociate in neutral aqueous solutions, but remains stable for at least five days at room temperature. ESI-MS also confirms the assigned stoichiometry of the anion (see the Supporting Information). Compound **1** is also soluble in methanol and ethanol, making it promising as a candidate for catalysis under a fairly wide range of conditions. Our primary synthetic target, $[N(CH_3)_4]_7[TiNb_9O_{28}]$, could not be separated from $[N(CH_3)_4]_8[Ti_2Nb_8O_{28}]$ as their crystal morphologies were too similar. While the original method of synthesis gave poor yields, the yields could be improved to over 50% **1** in the crystallized product, based on ESI-MS, by using stoichiometric amounts of each reagent, as detailed in the *Experimental Section*.

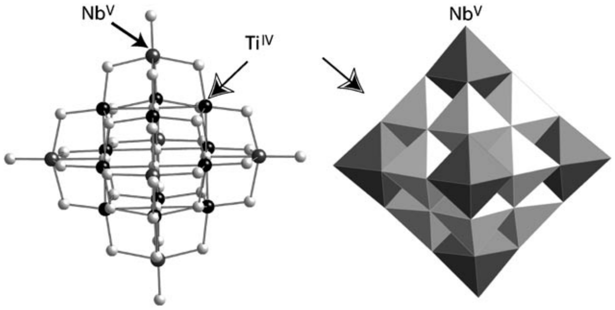

Figure 1. Ball-and-stick (left) and polyhedron (right) representations of $[Ti_{12}Nb_6O_{44}]^{10-}$ in **1**. The arrows identify titanium and niobium atoms.

While our targeted Nyman-type titanoniobate ions $[N(CH_3)_4]_8[Ti_2Nb_8O_{28}]$ and $[N(CH_3)_4]_7[TiNb_9O_{28}]$ are isostructural to the known decavanadate[4] and decaniobate[5,6] ions, the novel species **1** consists essentially of a cubic $[Ti_{12}O_{14}]^{20+}$ core (Figure 2), of which each face is capped by a $[NbO_5]^{5-}$ unit. This makes the overall structure hexagonal, so that **1** is a kind of "super-Lindqvist" ion. The decatungstate ion $[W_{10}O_{32}]^{4-}$ has a similar but simpler arrangement, in which two $[W_5(\eta\text{-O})_5(\mu_2\text{-O})_8(\mu_5\text{-O})]^{2+}$ fragments are connected through four μ_2-O bridges, also yielding a central cavity.[7]

Figure 2. Wireframe representation of the central $[Ti_{12}O_{14}]^{20+}$ core. Titanium and oxygen atoms in light and dark grey, respectively.

In **1**, the cavity measures about 4.3 Å across, and appears to be essentially vacant. X-ray diffraction data allowed for calculating the maximum occupancy for different potential guest atoms—two of the top four peaks, both representing approximately 1.4 e$^-$, in the final difference Fourier map were found to lie on special positions at the center of the complex. These two peaks were refined and found to correspond to a niobium occupancy of approximately 2%, which equals less

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[**] We are grateful to Drs. May Nyman and Travis M. Anderson for a gift of hydrous niobium oxide and generous advice. This project was funded by a grant from the US Department of Energy, Office of Basic Energy Science through DE-FG02-05ER15693 and the US National Science Foundation through EAR-0515600.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200801883.

Table 1: Selected bond lengths and angles in **1**, $[Ti_2Nb_8O_{28}]^{8-}$, and $[Nb_{10}O_{28}]^{6-}$ (see Figure 3). $[Nb_{10}O_{28}]^{6-}$ data from CSD-419971,[9] and data of $[Ti_2Nb_8O_{28}]^{8-}$, the Nyman-type titanoniobate, from reference [2].

Bond	**1**[a]	$[Ti_2Nb_8O_{28}]^{8-}$[a]	$[Nb_{10}O_{28}]^{6-}$[b]
Length [Å]			
A-O1	1.767(5)	1.751(18)	1.7410(12)
A-O2	2.035(5)	2.0323(18)	2.093(12)
A-O3,4,5	2.004(5)–2.025(5)	1.9689(18)–1.9892(19)	1.9631(11)–1.9913(11)
A-O8	2.304(5)	2.4638(19)	2.5341(11)
B-O2	1.829(5)	1.8167(18)	1.8405(12)
B-O6	1.829(5)	1.8242(18)	1.8335(12)
B-O7,9	1.940(5)–1.946(5)	1.9992(18)–2.0013(18)	2.0033(11)–2.0135(11)
B-O8	2.200(5)	2.1495(18)	2.215(11)
Angle [°]			
O1-A-O2	104.1(2)	103.60(8)	102.50(5)
O1-A-O8	178.8(2)	179.13[c]	176.09(5)
A-O2-B	110.3(2)	112.60[c]	113.29(6)
A-O8-B	89.57(16)	86.44[c]	86.88(4)
O2-B-O10	171.4(2)	166.89[c]	163.59(5)

[a] $A = Nb^{5+}$, $B = Ti^{4+}$ [b] $A = B = Nb^{5+}$. [c] Estimated standard deviation unavailable.

than one electron. Based upon charge-balance considerations in the crystal structure, we conclude that this central position is vacant. This conclusion is supported by the ESI-MS data, which show that the cluster anion really is $[Ti_{12}Nb_6O_{44}]^{10-}$. It is, however, not difficult to imagine that inclusion compounds may be synthesized as the cavity is sufficiently large to accommodate atoms as big as niobium.

In common with $Na_8[Ti_2Nb_8O_{28}]$, there are no terminal Ti–O bonds in **1**, which is not surprising based on observations by other groups.[8] The cluster contains 6 μ_5-O, 8 μ_3-O, 24 μ_2-O, and 6 η-O atoms, with each titanium atom being coordinated to 2 μ_2-O, 2 μ_3-O, and 2 μ_5-O atoms. The result of this arrangement is that, with the exception of the μ_5-O atoms, all oxygen atoms are exposed on the surface of the cluster and accessible to cationic counterions.

The M–O bonds in the cluster tend to alternate in a regular fashion between long and short bonds by about 0.02 to 0.04 Å (see the Supporting Information), which stems from the distortion of the preferentially octahedral $[NbO_6]^{7-}$ and $[TiO_6]^{8-}$ building blocks through displacement of the central metal atom off-center (Figure 3, Table 1). Whereas the apical Nb–μ_5-O bonds in **1** are contracted in comparison with the Nb–μ_6-O bonds in the Nyman-type titanoniobates and in decaniobate, the Ti–μ_5-O bond is quite similar to the Ti–μ_6-O and Nb–μ_6-O bonds in the latter ions. The terminal Nb–O bonds have lengths around 1.75 Å, that is, they are somewhat longer than those found in the other two ions, but similar to those found in hexaniobate.[9] The niobyl oxygen atoms in hexaniobate are difficult to protonate, which may also be true in **1**.

Discovery of this new POM type is timely because of the interest in photocatalytic oxidation of water, but also because it is among only a few classes of POMs with a central cavity. The group of Peter Burns has recently described several large actinyl–peroxide ions that have central cavities,[10] but these are structurally distinct from our cluster $[Ti_{12}Nb_6O_{44}]^{10-}$. We are now exploring possible other substitutions that can be made into this new POM, including Zr^{IV} and Hf^{IV} for Ti^{IV} and Ta^{V} for Nb^{V} and whether the molecule can be ^{17}O-enriched for rate studies,[6] which would make it possible to elucidate the reaction dynamics in water. This molecule, if it has the anticipated broad range in pH stability, could be an extraordinarily useful cluster to detail reaction pathways in water because it is structurally simple and is small enough for high-level computer simulations.

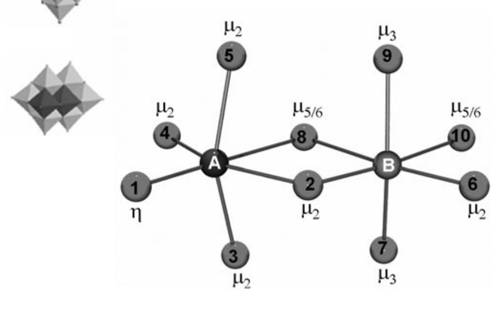

Figure 3. Ball-and-stick representation of adjacent octahedra in **1**, $[Ti_2Nb_8O_{28}]^{8-}$, and $[Nb_{10}O_{28}]^{6-}$ (the relevant moieties are shaded in the insets). See Table 1 for bond lengths and angles.

Experimental Section

Hydrous niobium oxide (350 mg; water content 43% w/w) and titanium isopropoxide (0.3 cm^3) were added to a solution of $[N(CH_3)_4]OH{\cdot}5H_2O$ (500 mg) in water (8 cm^3). The mixture was heated at 200 °C for about 20 h, yielding a clear solution. The solvent was removed in vacuo, affording a viscous oil, to which methanol (50 cm^3) was added. The TiO_2 flocculate that formed was removed by gravity filtration through paper. The solvent was removed in vacuo and the obtained oil allowed to crystallize over two weeks. The product, as indicated by ESI-MS, consisted mainly of rhombic crystals of $[NMe_4]_8[Ti_2Nb_8O_{28}]$ and $[NMe_4]_7[TiNb_9O_{28}]$. Twinned, approximately orthogonal crystals of **1** were isolated by hand under the microscope. The final structure refinement converged with $R(F) = 0.0649$, $wR(F2) = 0.1368$, GOF = 1.105 for all 25771 reflections ($R(F) = 0.0518$, $wR(F2) = 0.1302$ for those 22621 data with $F_o > 4\sigma(F_o)$). The crystals belong to space group $P2_1/c$, with $a = 27.056(2)$, $b = 26.190(2)$, $c = 16.7920(14)$ Å, $\alpha = 90$, $\beta = 93.610(2)$, $\gamma = 90°$.

We have since tried to optimize the synthesis, improving the apparent yield of **1** to around 50% of the obtained product, by following the general protocol described above, but using 0.50 g hydrous niobium oxide, 0.66 g $[N(CH_3)_4]OH{\cdot}5H_2O$, and 1.3 cm^3 titanium isopropoxide. See the Supporting Information for ESI-MS spectrum, micrographs of a single crystal of **1**, and structure-acquisition and -refinement parameters. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax:

(+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-419424.

Received: April 22, 2008

Keywords: cluster compounds · oxides · polyoxometalates · structure elucidation

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