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Polyoxoniobates

The Construction of High-Nuclearity Isopolyoxoniobates with Pentagonal Building Blocks: $[HNb_{27}O_{76}]^{16-}$ and $[H_{10}Nb_{31}O_{93}(CO_3)]^{23-}$**

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Polyoxometalates (POM) are metal oxide cluster compounds with applications in many fields from medicine to nanotechnology.[1] The wide interest and numerous applications mean that the development of POM clusters beyond the traditional molybdenum-, tungsten-, and vanadium-based building blocks is important. The development of polyoxoniobates is still at an early stage and has built upon the isopolyoxoniobate $[Nb_6O_{19}]^{8-}$ ion reported by Lindqvist[2] along with the $[Nb_{10}O_{28}]^{6-}$,[3] $[Nb_{20}O_{54}]^{8-}$,[4] and $[H_9Nb_{24}O_{72}]^{15-}$ ions.[5] Also, the discovery of the first heteropolyanion,[6] a $\{Nb_{12}\}$ Keggin-like structure ($\{[Ti_2O_2][SiNb_{12}O_{40}]\}^{12-}$) by Nyman et al. and the recent developments presented by Casey and co-workers[7] demonstrate that Nb-based POMs have great potential.[6–10] However, the expansion of the field of polyoxoniobates is severely limited by the difficulty in controlling the synthesis. In particular, the narrow window of pH values for solution polyoxoniobate chemistry lies around 10.5–12.5 for reactions under ambient conditions.[5] Given these difficulties, there is a need to develop new approaches to extended polyoxoniobate-based architectures, which is especially important owing to their unique basic properties and potential for catalysis, for example in water splitting.[11]

Herein we report the synthesis and structural characterization of two compounds **1** and **2**, which contain the polyoxoniobate anions $[HNb_{27}O_{76}]^{16-}$ (**1a**) and $[H_{10}Nb_{31}O_{93}(CO_3)]^{23-}$ (**2a**), respectively. To our knowledge, **1a** is the largest isopolyoxoniobate cluster reported to date, while **2a** is even bigger than **1a**, but with carbonate ion coordinated on the outside of the cluster; cluster **2a** is also intrinsically chiral. Furthermore, structural analysis by single-crystal X-ray crystallography reveals that both of these polyoxoniobates are unprecedented, as they are built from pentagonal $\{Nb(Nb)_5\}$ building units.

$K_{13}Na_3{\cdot}\mathbf{1a}{\cdot}25\,H_2O$ (**1**) and $K_{19}Na_4{\cdot}\mathbf{2a}{\cdot}35\,H_2O$ (**2**) are prepared in similar syntheses under hydrothermal conditions using $K_7HNb_6O_{19}{\cdot}13\,H_2O$[12] as the precursor in the presence of sodium dibenzyldithiocarbamate. Slow vapor diffusion of methanol into the aqueous solution gave single crystals of $K_{13}Na_3{\cdot}\mathbf{1a}{\cdot}25\,H_2O$ (hexagonal blocks), while $K_{19}Na_4{\cdot}\mathbf{2a}{\cdot}35\,H_2O$ (blocks) is crystallized by slow evaporation of the mother liquor after it was subjected to the hydrothermal conditions. Compound **1** contains the $[HNb_{27}O_{76}]^{16-}$ cluster of C_{3v} symmetry (Figure 1), which itself incorporates three pentagonal $\{(Nb)Nb_5\}$ units. These building blocks are unknown in isopolyoxoniobate chemistry, yet they have great potential for the assembly of spherical clusters with very high nuclearity.[13–15] In each of the pentagonal building blocks, the central Nb atom is coordinated by seven oxo ligands in a pentagonal-bipyramidal geometry.

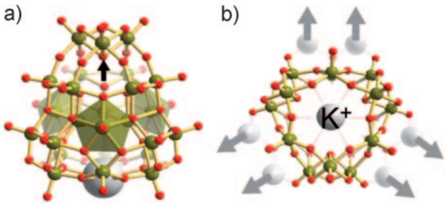

Figure 1. Ball-and-stick representation of the structure of **1a**. a) View of the entire cluster highlighting the pentagonal units using a polyhedral representation. The arrow points to the protonated O atom. b) View from the base of the cluster containing the complexed potassium ion in a $\{Nb_6O_6\}$ "crown ether". The gray arrows emphasize the direction of framework growth. (Nb green, O red, K gray)

Such pentagonal units are quite rare. They have only been observed in $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ [13] and in the family of mixed valence gigantic Mo wheel-shaped and spherical Keplerate clusters[14] pioneered by Müller and co-workers.[14,15] Further pentagonal units have recently been observed in mixed molybdenum/tungsten-based POM Keplerates, whereby the pentagonal $\{M(M)_5\}$ units are tungsten-based.[15] From an architectural point of view, pentagonal building units play an important role in forming large spherical or ring clusters or curved frameworks, similar to fullerenes, which consist of hexagonal and pentagonal building blocks. This motif could potentially prove to be extremely important for the development of larger spherical Nb-based polyoxoniobates parallel to the uranium-based POM systems.[16]

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The main building block present in the $\{Nb_{27}\}$ cluster in **1a** is comparable to the metal oxo cage found in the α-Keggin structure,[6] and three pentagonal subunits encapsulate this moiety (Figure 2). Bond valence sum (BVS) analysis of compound **1** suggests that the μ_3-oxo ligand that bridges the three metal atoms which form the cap of the $\{M_{12}\}$ subunit is protonated (Figure 1), and this proton occupies the cavity in which a heteroatom is normally found in the case of the discrete $\{Nb_{12}\}$ cluster.[6,10] At the base of the cluster, a Nb/O-based 12-membered metallacrown-like moiety, $\{Nb_6O_6\}$, complexes a potassium cation (Figure 1b). Such crown ether moieties are known in POM chemistry[17] but are unknown in polyoxoniobate chemistry. A view of the solid-state structure of compound **1** looking down the *c* axis into the *ab* plane is presented in Figure 3, and it can be seen that **1** forms a hexagonal extended network layer through $K\cdots O_t$ (terminal oxo on $\{Nb_{27}\}$ cluster) electrostatic interactions. The honeycomb layers are stacked in a head-to-tail fashion through $K\cdots O_t$ interactions, forming 1D channels parallel to the crystallographic *c* axis. The diameter of the channels is approximately 1.7 nm, and they also contain a severely disordered $\{Nb_n\}$ cluster. The arrangement of heavy atoms suggests that $\{Nb_n\}$ is similar to the above well-defined $\{Nb_{27}\}$ cluster (see the Supporting Information).

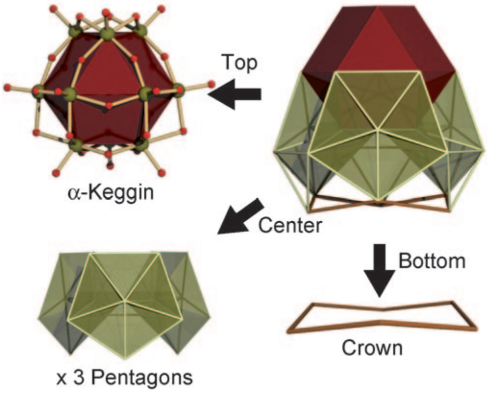

Figure 2. Schematic depiction (metal framework shown) of **1a** showing the $\{Nb_{27}\}$ cluster featuring three parts: an α-Keggin-like structure on top (red polyhedra) fused to three pentagonal units, and a crown ether ring moiety in the base of the cluster.

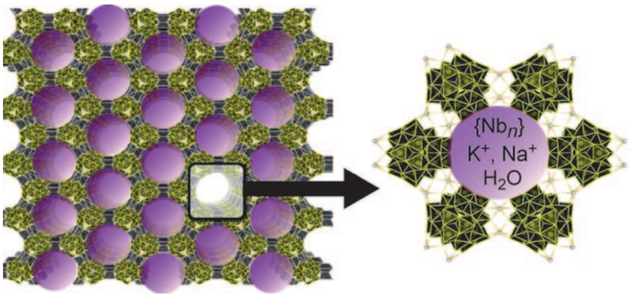

Figure 3. Packing view along the *c* axis of **1**. Green polyhedra represent Nb; purple highlights channels containing counterions, disordered $\{Nb_n\}$ clusters, and water.

The structure of the $[H_{10}Nb_{31}O_{93}(CO_3)]^{23-}$ cluster **2a** is shown in Figure 4. Interestingly, the structure of **2** contains two independent clusters in the asymmetric unit, and each cluster is fully occupied. Ignoring the CO_3^{2-} part, the cluster framework of **2a** has essentially C_2 symmetry. With the coordination of CO_3^{2-}, the whole cluster does not have any symmetry element, and therefore the cluster itself is chiral. Both enantiomers are present in the unit cell, giving a racemic material.

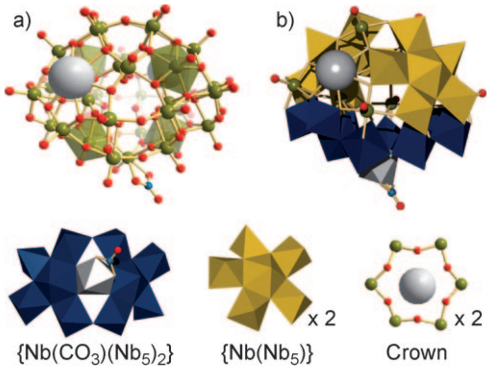

Figure 4. Structure of **2a**. a) Ball-and-stick view (Nb green, O red, K gray, C blue) and b) pentagonal representation. Blue and yellow polyhedra show $\{Nb(CO_3)(Nb_5)_2\}$ and $Nb(Nb)_5$ building blocks, respectively; gray polyhedra represent the CO_3^{2-}-coordinated Nb system.

Cluster **2a** has four pentagonal $\{Nb(Nb)_5\}$ building units similar to those found in **1a**. Two $\{Nb(Nb)_5\}$ building blocks (yellow polyhedra) and one $\{Nb(CO_3)(Nb_5)_2\}$ (blue and gray polyhedra; two $\{Nb(Nb)_5\}$ units share one Nb center that coordinates to CO_3^{2-}) are connected by several Nb linkers, which themselves form metallacrown-type $\{Nb_6O_6\}$ units.

In this case, two $\{Nb_6O_6\}$ units on opposite sides of the cluster cage each bind a potassium ion. Furthermore, while both clusters **1a** and **2a** can be classified as polyoxoanions, **2a** also contains a bidentate CO_3^{2-} ligand, as confirmed by infrared spectroscopy, which clearly shows a band associated with the CO_3^{2-} ion (see Figure S5 in the Supporting Information). This moiety is coordinated to one Nb center to give a seven-fold coordinated geometry, so that the Nb center is ligated to one terminal oxo ligand (Nb=O), the bidentate CO_3^{2-} ion, and to four bridging oxo ligands connected to adjacent Nb centers in the cluster. In this cluster, BVS analysis suggests that there are six protonated oxo ligands and two coordinated water molecules. All the protonated O atoms are positioned on the inner side of the cluster along with the two water molecules, which appear to be encapsulated by the cluster framework (see also the Supporting Information).

It is interesting to note that cluster **2a** contains one CO_3^{2-} ligand. The pH value of the solution after the hydrothermal reaction is around 10, therefore the absorption of CO_2 will generate carbonate. Furthermore, upon standing in air, the pH value of the solution decreases to 9,[18] thus indicating sequestration of CO_2 by the reaction mixture. On the whole, the solution chemistry of the polyoxoniobates is extremely complex and very sensitive to the reaction conditions, which make analysis and the development of new synthetic routes extremely difficult. Furthermore, the conditions which allow the formation of compounds **1** and **2** are very similar, and these ultimately result in polymerization of the building blocks to an ilmenite structure, or $MNbO_3$ ($M = Na^+, K^+$, etc.; Figure 5). Normally, $MNbO_3$ ilmenite is obtained from a hydrothermal reaction (100–300 °C for 3–7 days) of $\{Nb_6\}$ in the presence of a base[19] and can also be obtained by evaporation of a solution of $\{Nb_6\}$ species under a CO_2 atmosphere.[20] In our case, it qualitatively appears that the $\{Nb_{27}\}$ and $\{Nb_{31}\}$ species are only isolated in the presence of dibenzyldithiocarbamate; this conclusion is confirmed by control reactions without dibenzyldithiocarbamate, which do not produce compounds **1** or **2**.

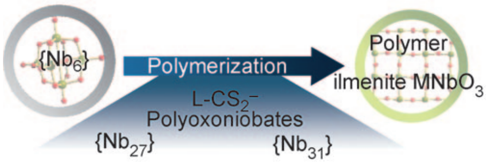

Figure 5. Representation of the formation of compounds **1** and **2** from a hydrothermal synthesis incorporating sodium dibenzyldithiocarbamate.

To explore the reaction system shown in Figure 5 in more detail, we conducted the hydrothermal experiment over 20 h, with $\{Nb_6\}$ as the precursor, and then treated the mother liquor with hexadecyltrimethylammonium bromide. This procedure was intended to produce a material that could be dissolved in acetonitrile for analysis by high-resolution ESI-MS.[21,22] These experiments resulted in the observation of a range of envelopes that can be assigned to $\{Nb_6\}$, $\{Nb_{10}\}$, $\{Nb_{20}\}$, and $\{Nb_{27}\}$ (Figure 6). Although the $\{Nb_6\}$ is still present as the main component, it is possible to identify unambiguously a range of species that can be assigned as the $\{Nb_{27}\}$-based anions present in compound **1**. This finding clearly indicates that the dibenzyldithiocarbamate is required to form larger quantities of compound **1**, but that it is not mechanistically essential.

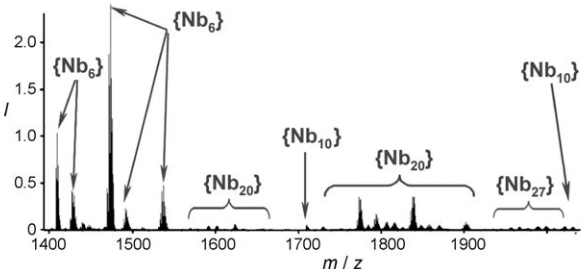

Figure 6. ESI mass spectrum of the Nb-based species obtained by hydrothermal reaction of $\{Nb_6\}$ in the absence of sodium dibenzyldithiocarbamate after 20 h at 200 °C. Measurements were performed using ion-exchanged hexadecyltrimethylammonium salts in a mixed H_2O/MeCN solvent.

In summary, two unprecedented polyoxoniobate compounds were isolated and structurally characterized by subjecting $\{Nb_6\}$ to hydrothermal conditions in the presence of sodium dibenzyldithiocarbamate. Both clusters **1a** and **2a** are the largest isopolyniobates reported to date and employ pentagonal building units in their respective architectures, which opens up a range of perspectives for the development of much larger, more spherical cluster architectures. Furthermore, the cluster **2a** binds a CO_3^{2-} ion, and the cluster is itself chiral. These unique types of polyoxoniobates unveil the potential for further developments of polyoxoniobate chemistry, and the sensitivity of the reaction to the presence of 'spectator' ligands is interesting and important. In further work, we will explore the ligand dependence on the formation of compounds **1** and **2** in more detail to establish the applicability of this synthetic procedure, as well as expanding the number of Nb-based POMs to produce much larger architectures that take advantage of the pentagonal building blocks. Finally, the observation of the cluster **1a** found in compound **1** using ESI-MS, without the additive ligand required to isolate the material, demonstrates the power and potential of mass spectrometry as a tool in the discovery of fundamentally new cluster archetypes.[22]

Experimental Section

$K_7HNb_6O_{19}\cdot 13\,H_2O$ (1.0 g, 0.73 mmol) and sodium dibenzyldithiocarbamate (0.4 g, 1.4 mmol) were dissolved in water (8 mL) and placed in a Teflon autoclave. The resulting mixture was placed in an oven and heated to 200 °C for three days before cooling to room temperature (Caution: Noxious fumes arising from decomposition of dibenzyldithiocarbamate are produced, which might originate from formation of CS_2 and S_8. Single crystals of the later were also obtained) and filtered to remove white amorphous material (ca. 0.7 g). Crystallization of compounds **1** and **2** from the mother liquor was achieved as follows. Compound **1**: Slow diffusion of methanol into the mother liquor at room temperature resulted in 0.2–0.3 g of material, from which hexagonal colorless crystals of **1** (ca. 30 mg)[23] were separated from a mixture of smaller crystals of **1** and plate crystals of $\{Nb_6\}$. Compound **2**: Slow evaporation of a solution in air resulted in ca. 0.2–0.3 g of material, from which square plate-like crystals of **2** (ca. 10 mg) were separated from a mixture of smaller crystals of **2**[23] and plate crystals of $\{Nb_6\}$, which formed over a period of one week. Furthermore, compound **1** could also be produced by slow evaporation, but compounds **1** and **2** were never seen together in the same batch. Note that the yields are difficult to quantify precisely owing to crystal dehydration upon removal of solvent and to impurity of the $\{Nb_6\}$ starting materials. Efforts to optimize the reaction procedure as well as the yield of the two products are under way. Preliminary elemental analysis was performed by EDX-SEM with single crystals of **1** and **2**, which allowed high-quality analysis without contamination from impurities such as $\{Nb_6\}$. The estimated formula of **1** is $(K_{13}Na_3)[HNb_{27}O_{76}]\cdot 25\,H_2O$ and of **2** is $(K_{19}Na_4)[H_{10}Nb_{31}O_{93}(CO_3)]\cdot 35\,H_2O$. Full details are given in Supporting Information along with analysis combining the analytical and structural data.

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[23] $K_{13}Na_3HNb_{27}O_{76}{\cdot}25\,H_2O$ **1**: $H_{51}K_{13}Na_3Nb_{27}O_{101}$, $M_r = 4753.25\ \mathrm{g\,mol^{-1}}$, block crystal, $0.11 \times 0.11 \times 0.05\ \mathrm{mm^3}$, $T = 150(2)$ K, monoclinic, space group Cm, $a = 24.3719(10)$, $b = 42.3264(18)$, $c = 16.0098(9)$ Å, $\beta = 98.776(6)°$, $V = 16\,321.9(13)$ Å^3, $Z = 6$, $\rho = 2.901\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Cu_{K\alpha}}) = 27.881\ \mathrm{mm^{-1}}$, $F(000) = 13\,476$, 40925 reflections measured, 18027 unique ($R_{int} = 0.0382$), 1769 refined parameters, $R1 = 0.0747$, $wR2 = 0.2113$. One $\{Nb_{27}\}$ cluster was well-defined, and a half cluster was found disordered over a crystallographic mirror plane. However, from the arrangement of heavy atoms found, the cluster could be recognized as $\{Nb_{27}\}$, similar to the previous well-defined cluster. K^+, Na^+, and solvent water molecules were partially located. The final formula was determined on the basis of elemental analysis of Nb/K/Na. $K_{19}Na_4H_{10}Nb_{31}O_{93}$-$(CO_3){\cdot}35\,H_2O$ **2**: $CH_{80}K_{19}Na_4Nb_{31}O_{131}$, $M_r = 5903.72\ \mathrm{g\,mol^{-1}}$, block crystal, $0.08 \times 0.05 \times 0.04\ \mathrm{mm^3}$; $T = 150(2)$ K, monoclinic, space group $P2_1/c$, $a = 27.7849(2)$, $b = 36.6259(3)$, $c = 28.8773(2)$ Å, $\beta = 100.8920(10)°$, $V = 28\,857.5(4)$ Å^3, $Z = 8$, $\rho = 2.718\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Cu_{K\alpha}}) = 25.350\ \mathrm{mm^{-1}}$, $F(000) = 22\,480$, 176937 reflections measured, 45800 unique ($R_{int} = 0.0552$), 3006 refined parameters, $R1 = 0.0487$, $wR2 = 0.1238$. Two $\{Nb_{31}\}$ clusters were found in the asymmetric unit. Each cluster contains a disordered Nb center (Nb63 and Nb64, respectively). All other atoms on the clusters were well-defined. K^+, Na^+, and solvent water molecules were partially located. The final formula was determined on the basis of elemental analysis of Nb/K/Na in combination with structural arguments. Crystal data were measured on a Oxford Diffraction Gemini CCD diffractometer using $\mathrm{Cu_{K\alpha}}$ radiation ($\lambda = 1.54184$ Å) at 150(2) K. CSD 420848 (**1**) and CCDC 740453 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax. (+49)7247808666; e-mail: crysdata @fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) and The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.