



**[SiNb<sub>12</sub>O<sub>40</sub>]<sup>16-</sup> and [GeNb<sub>12</sub>O<sub>40</sub>]<sup>16-</sup>: New Highly Charged Keggin Ions with Sticky Surfaces**

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CH-1346

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## Introduction

Heteropolyanions are negatively-charged clusters of corner-sharing and edge-sharing early transition metal MO<sub>6</sub> octahedra and heteroatom XO<sub>4</sub> tetrahedra, where the tetrahedra are usually located in the interior of the cluster.<sup>[1]</sup> The geometry, composition, and charge of these clusters are varied through synthesis parameters, and cluster properties are highly tunable as a function of these characteristics. Heteropolyanions have been employed in a range of applications that include virus-binding inorganic drugs,<sup>[2]</sup> homogeneous and heterogeneous catalysts,<sup>[3, 4]</sup> electro-optic and electro-chromic materials,<sup>[5, 6]</sup> metal and protein binding,<sup>[7]</sup> and as building blocks for nano-structuring of materials<sup>[8]</sup>. The  $\alpha$ -Keggin geometry, which was first structurally characterized in 1933 by J.F. Keggin<sup>[9]</sup> for the phosphotungstic acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) is one of the most widely recognized and thoroughly studied heteropolyanion geometries.<sup>[10]</sup> Presented here is the first synthesis and structural characterization of the dodecaniobate Keggin ion in the form of a water-soluble salt containing isolated clusters. To our knowledge, the [TNb<sub>12</sub>O<sub>40</sub>]<sup>16-</sup> (T = Si, Ge) Keggin ions reported herein have the highest negative charge observed for clusters possessing the plenary Keggin geometry; and also higher charge than the typical mono-, di- and trivacant lacunary Keggin ions. The unprecedented high charge should render these clusters unique with regard to metal binding and other applications involving anion-cation electrostatic interactions in solution or at interfaces.

These [TNb<sub>12</sub>O<sub>40</sub>]<sup>16-</sup> clusters (T = Si, Ge) Na<sub>16</sub>[SiNb<sub>12</sub>O<sub>40</sub>] $\cdot$ 4H<sub>2</sub>O (**1**) and Na<sub>16</sub>[GeNb<sub>12</sub>O<sub>40</sub>] $\cdot$ 4H<sub>2</sub>O (**2**) are chemically quite different from the related heteropolymolybdate and heteropolytungstate Keggin ions in their synthetic approach, their pH stability, as well as their charge. The Nb-Keggin ions are synthesized and stable in basic solutions (pH~7-12.5) and decompose in acidic solutions, whereas the Mo- and W- Keggin ions are synthesized and stable in acidic solutions (~ pH=1-3) and decompose in more basic solutions.

## Experimental

From the microcrystalline powder of **1**, an approximately cube-shaped crystal with a 15-micron diameter was selected for single-crystal X-ray diffraction data collection at ID11. The experimental conditions are summarized as follows:  $\lambda = 0.50915 \text{ \AA}$ ,  $T = 295 \text{ K}$ ; cubic system, space-group  $P-43n$ ,  $a = 20.5185(16) \text{ \AA}$ ,  $V = 8638.5(12) \text{ \AA}^3$ ,  $Z = 8$ ,  $\rho_{\text{calc}} = 3.41 \text{ g cm}^{-3}$ ,  $\mu = 10.42 \text{ mm}^{-1}$ ,  $F(000) = 8272$ ; 34707 measured reflections, of which 3505 were independent ( $R_{\text{int}} = 0.049$ ). Refinement on  $F^2$ , 206 parameters refined, Flack parameter  $x = 0.108(23)$ ;  $R1 = 0.0503$  for 3313  $F_{\text{obs}} > 4 \sigma(F_{\text{obs}})$  and  $R1 = 0.0530$  for all 3505 data,  $wR2 = 0.1436$ , goodness of fit  $S = 1.049$ . Residual electron density:  $+2.54/-1.47 \text{ e}^- \text{ \AA}^{-3}$ . Hydrogen atoms of water molecules were not located. Structure solution and refinement using Shelx97 [Programs for Crystal Structure Analysis (Release 97-2). G. M. Sheldrick, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.]. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: [crysdata@fiz-karlsruhe.de](mailto:crysdata@fiz-karlsruhe.de)) on quoting the depository number CSD-413539)

## Description of the structure

The structure of  $\text{Na}_{16}[\text{SiNb}_{12}\text{O}_{40}] \cdot 4\text{H}_2\text{O}$  **1** was solved in the cubic space group,  $P-43n$ . The single-crystal data of **1** reveals two crystallographically distinct  $[\text{SiNb}_{12}\text{O}_{40}]^{16-}$   $\alpha$ -Keggin ions in the unit cell. Fig. 1 shows the two Keggin ions in a ball-and-stick model. The  $\text{Nb1O}_6$  octahedra of Keggin-1 and the  $\text{Nb2O}_6$ ,  $\text{Nb3O}_6$  and  $\text{Nb4O}_6$  octahedra of Keggin-2 are distorted in the regular fashion of polyoxometalate  $d^0$  metals with a long axial  $\text{Nb-O}_c$  bond to the

center of the cluster ( $2.395(7) - 2.49(1) \text{ \AA}$ ), a short axial  $\text{Nb-O}_t$  terminal bond (ranging from  $1.735(9)$  to  $1.778(8) \text{ \AA}$ ) to the outside of the cluster, and four intermediate equatorial  $\text{Nb-O}_b$  bonds (between  $1.92(1)$  and  $2.03(1) \text{ \AA}$ ).

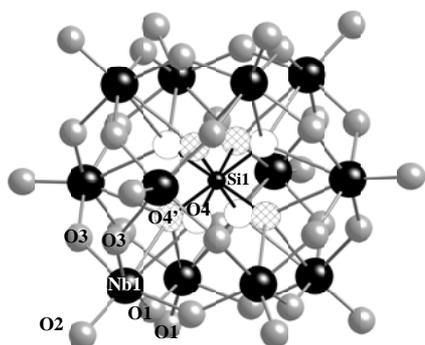
With further study, the high negative charge of these new heteropolyniobates may be

exploited for greater selectivity or strength of binding in applications that utilize the electrostatic interaction between negatively charged polyoxometalate clusters and positively-charged species or species featuring positively charged regions (i.e. amino acids, proteins, metals, viruses).

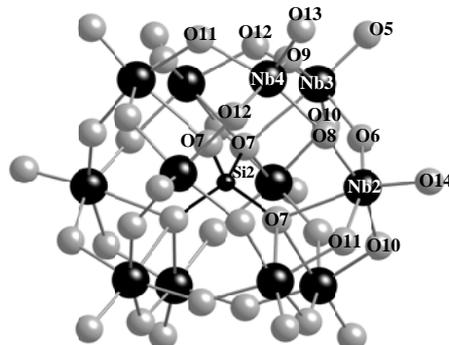
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Keggin-1



Keggin-2



**Fig. 1.** Ball-and-stick representation of the two crystallographically unique Keggin ions of **1**.