A Supramolecular Tetra-Keggin Polyoxometalate $[Nb_4O_6(\alpha\text{-}Nb_3SiW_9O_{40})_4]^{20-}$**

Gyu-Shik Kim, Huadong Zeng, Don VanDerveer, and Craig L. Hill*

The self-assembly of modular and multicomponent inorganic systems into larger structures or materials with useful properties remains an intense focus of current research.[1] In this context, the formation of giant polyoxometalates (POMs) with catalytic, magnetic, and antiviral properties in part attributable to their structures, is of interest.[2] Herein we explore the acid-induced formation of Nb-O-Nb linkages between Nb-containing POM units to generate supramolecular poly(POM) species,[3–6] and report the synthesis and characterization of a structurally novel tetrameric Keggin complex, **1**. The stability of this complex is also evaluated under physiological conditions, because the corresponding well-studied monomer **2** and dimer **3**[3] are some of the least toxic and most potent antiviral agents of the 300+ POMs investigated biologically and pharmacologically.[7–12]

$[Nb_4O_6(\alpha\text{-}Nb_3SiW_9O_{40})_4]^{20-}$ **1**

$[Nb_3SiW_9O_{40}]^{7-}$ **2**

$[Nb_6Si_2W_{18}O_{77}]^{8-}$ **3**

Reaction of $Nb_6O_{19}^{8-}$ and aqueous peroxide H_2O_2 with solid $\alpha\text{-}SiW_9O_{34}^{10-}$ forms **1** in 51% yield. If the Keggin units used in the synthesis already contain the requisite three Nb atoms, the yield of **1**, not surprisingly, is higher. For example, reaction of $Nb_6O_{19}^{8-}$ and aqueous H_2O_2 with the triperoxo compound $\alpha\text{-}Cs_6H[(NbO_2)_3SiW_9O_{37}]$ (Cs-**4**) as a solid affords **1** in 81% yield. Both reactions proceed with vigorous evolution of O_2. The attempt to prepare **1** by initial construction of the $Nb_4O_6^{8+}$ unit (controlled hydrolysis of $Nb(OEt)_5$ under acidic conditions) followed by addition of **4** produces only the known tri-μ-oxo dimer **3**.[3] The stoichiometry, selection of appropriate POM synthons (tectons), and good structural fit between the $Nb_4O_6^{8+}$ unit and the Keggin POM units appear to be responsible in part for the successful synthesis. The nBu_4N salt of **1** is easily prepared by metathesis of the Cs salt at low pH.

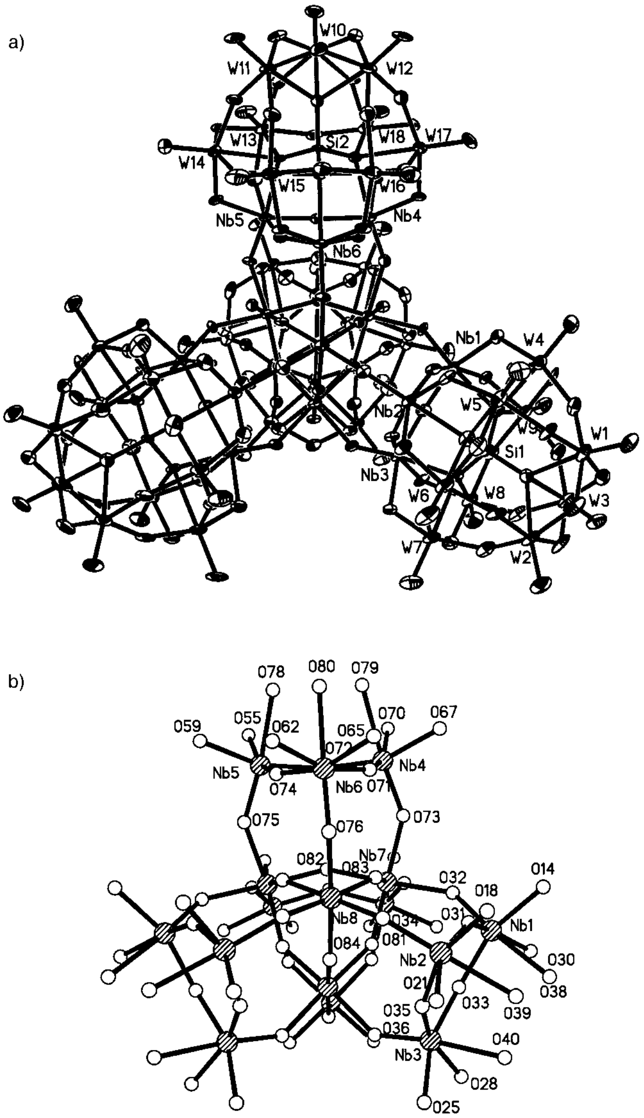

Figure 1. ORTEP drawings of the structure of Cs-**1**. a) View down the pseudo-C_3 axis of **1**. b) View of the $Nb_{16}O_{66}$ core. Selected average bond lengths [Å] and angles [°]: Nb(K)–O_{b1} 1.84(1), Nb–O_{b2} 1.93(1), Nb–O_{b3} 2.02(1), Nb(C)–O_{b1} 2.06(1), Nb–O_{b4} 1.94(1); Nb-O_{b1}-Nb 139.7(7), Nb-O_{b2}-Nb 148.5(5), Nb-O_{b4}-Nb 141.5(9); where O_{b1} is a doubly bridging oxygen atom between the Keggin unit and the Nb_4O_6 core; O_{b2} is a doubly bridging oxygen atom between Nb atoms in the Keggin unit; O_{b3} is a doubly bridging oxygen atom between Nb and W atoms in the Keggin unit; O_{b4} is a doubly bridging oxygen atom between Nb atoms in the Nb_4O_6 core; Nb(K) are Nb atoms in the Keggin unit, and Nb(C) are Nb atoms in the Nb_4O_6 core.

Single crystals of Cs-**1** were found to be suitable for X-ray crystallography;[13] Figure 1 shows the structure of the C_2 tetra-Keggin polyanion **1** and its $Nb_4O_6^{8+}$ core. Each of the four $\alpha\text{-}[Nb_3SiW_9O_{40}]^{7-}$ Keggin units are linked by three Nb-O-Nb bonds to one [Nb–O]$_3$ face of the $Nb_4O_6^{8+}$ tetrahedral core. A crystallographically imposed C_2 axis passes through two O atoms (O82 and O84) in the $Nb_4O_6^{8+}$ core; nonetheless, **1** and $Nb_4O_6^{8+}$ approach the maximum possible T_d symmetry. The M_4O_6 adamantanoid unit has been reported in several complexes,[14–18] and in one Nb_4 complex, $[(Cp^*Nb)_4O_4]$

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[**] This work was supported by the U.S. National Institutes of Health (R01 AI32903-04A1), and the Molecular Design Institute (Office of Naval Research, grant N00014-95-1-1116). We thank J. Cowan, J. Rhule, and Dr. S. Wu for the ^{183}W and ^{29}Si NMR spectra.

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

($Cp^* = C_5Me_5$).[16] However, the latter contains Nb^{IV} (d^1) centers unlike the Nb^V (d^0) centers in **1**. Alternatively, **1** may be viewed as four α-$SiW_9O_{34}^{10-}$ units supported on $Nb_{16}O_{30}^{20+}$, the largest isopolyniobate unit observed in a discrete molecule.

This tetrahedral complex of four Keggin units completes a structural series of increasing dimensionality and nuclearity: the double Keggin structure exemplified by tri-μ-oxo dimer **3** (a one-dimensional motif), the triple Keggin structure, exemplified only by $[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$[19] and a partially characterized Co analogue[20] (a two-dimensional motif), and **1**, a quadruple Keggin structure (a three-dimensional motif).

Four lines of direct or indirect evidence are consistent with maintenance of the solid-state structure of **1** (Figure 1) in aqueous solution (Figure 2). First, the ^{29}Si NMR spectrum (sharp singlet at $\delta = -85.04$) and the ^{183}W NMR spectrum (two singlets at $\delta = -127.6$ and -132.8 in a 2:1 integration ratio) are consistent with the approximate overall T_d symmetry of **1** and the local C_{3v} symmetry of each of the four pendant Keggin units (Figure 1). Second, the FT-IR spectrum of **1** in D_2O (35 mM Li-**1**) and in the solid state (Cs-**1** in KBr) are similar, and both exhibit a medium to strong Nb-O-Nb stretch at about $723 \pm 13\ cm^{-1}$ which precludes the presence of only monomer (see Figure S1 in the Supporting Information).[21] Third, the ^{183}W NMR chemical shifts of **1** are quite distinct from those of the monomer **2** and the dimer **3** under similar conditions, and fourth, both the ^{183}W NMR and FTIR spectra indicate that titration of **1** with the 24 equivalents of hydroxide forms **2** quantitatively (see Figure S2 in the Supporting Information).

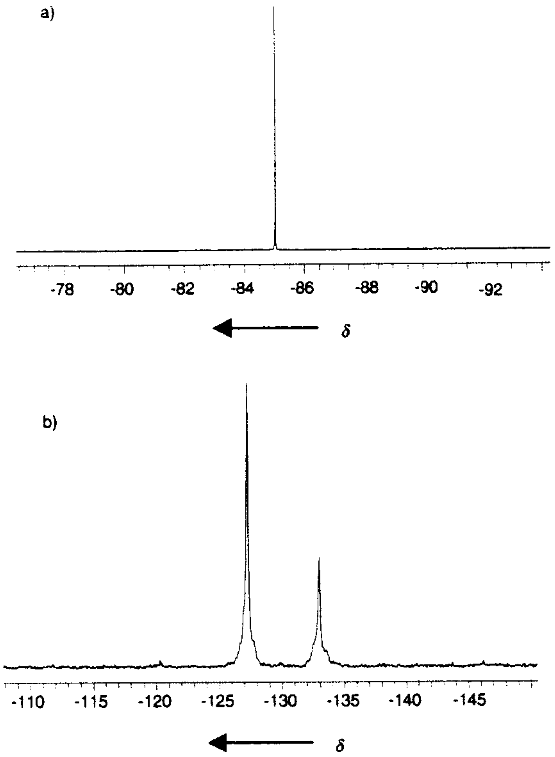

Figure 2. ^{29}Si NMR (a) and ^{183}W NMR (b) spectra of $Li_{20}[(Nb_4O_6)(\alpha\text{-}Nb_3SiW_9O_{40})_4]$ in D_2O (72 mM, pD = 0.6).

^{183}W NMR and FTIR establish that at pD values of 1.0, 4.2, and 6.0, respectively, **1** equilibrates to the following POMs: 100% **1**, 70% **1** plus 30% **2**, and 100% **2**. The cyclic voltammetric behavior of these Nb_3SiW_9-based species (**1**, **2**, and **3** all give quasi-reversible cyclic voltammograms at glassy carbon electrodes) is also consistent with the same pH-dependent speciation. These results make it clear that while **1** is thermodynamically stable at the pH of the stomach (pH 1–2), it is not at the pH of human serum (pH ~ 7.3).

The reduction potentials of **1** (pH = 0), **2** (pH = 4), and **3** (pH = 0) are −518, −706, and −664 mV versus Ag/AgCl, respectively. Neither H_2S nor NH_2NH_2 reduces **1** under anaerobic conditions at 25 °C in aqueous solution, and unlike several heteropoly anions, including the Nb-containing compounds $[Nb_3P_2W_{15}O_{62}]^{9-}$ and $[Nb_2W_4O_{19}]^{4-}$,[22] **1** does not catalyze the aerobic oxidation of sulfide ($H_2S + \frac{1}{2}O_2 \rightarrow \frac{1}{8}S_8 + H_2O$).[23]

Experimental Section

α-Cs-**4**: To a stirred solution of $K_7HNb_6O_{19} \cdot 13\,H_2O$[24] (1.91 g, 1.39 mmol) dissolved in aqueous H_2O_2 (250 mL of a 0.5 M solution) was added dropwise aqueous HCl (20 mL of a 1.0 M solution) followed by solid α-$Na_{10}SiW_9O_{34} \cdot 23\,H_2O$ (7.82 g, 2.72 mmol). To the resulting solution was added solid CsCl (25.0 g, 149 mmol). After 15 min of stirring, the orange-yellow precipitate was removed by filtration, washed with diethyl ether (2 × 20 mL) and dried in air to give 9.11 g of yellow powder (86.9% yield based on $Nb_6O_{19}^{8-}$). FT-IR (KBr pellet): $\tilde{\nu}$ [cm^{-1}]: 994 (w), 957 (m), 903 (vs), 868 (sh), 789 (vs), 673 (vw), 592 (w), 534 (w). 482 (vw); elemental analysis (%) calcd for $Cs_6H[(NbO_2)_3SiW_9O_{37}] \cdot 8\,H_2O$: H 0.48, Si 0.78, Cs 22.2, Nb 7.76, W 46.1; found: H 0.44, Si 0.62, Cs 21.9, Nb 7.50, W 46.5.

Cs_{20} salt of **1**: To a solution of $K_7HNb_6O_{19} \cdot 13\,H_2O$ (0.76 g, 5.5 mmol) in aqueous H_2O_2 (150 mL of a 0.5 M solution) was added HCl (20 mL of a 6.0 M solution). To this yellow solution was added α-Cs-**4** (12.76 g, 3.552 mmol) and $LiClO_4$ (2.47 g, 6.54 equiv) in HCl (35 mL of a 0.8 M solution) followed by removal of the $CsClO_4$ (0.10 g). The resulting mixture was refluxed for 3 h until the yellow color disappeared. After cooling to ambient temperature, CsCl (20.3 g) was added. After 30 min, the white precipitate was removed by filtration, washed with methanol (2 × 20 mL) and diethyl ether (2 × 20 mL), and dried in air overnight to give 10.46 g of a colorless crystals (81.0% yield based on α-Cs-**4**). FTIR (KBr pellet): $\tilde{\nu}$ [cm^{-1}]: 1003 (w), 963 (m), 920 (s), 785 (vs), 710 (s, Nb-O-Nb), 534 (w), 425 (vw); (in D_2O, AgBr windows): 1003 (w), 965 (m), 934 (s), 915 (s), 884 (vw, sh), 803 (s), 735 (m, Nb-O-Nb). ^{29}Si NMR (79.456 MHz, 0.8 M HCl/D_2O, $+LiClO_4$, $-CsClO_4$; 1.6 M NaTMSPA (TMSPA = trimethylsilylpropionate in D_2O standard): $\delta = -85.04$ (fwhh = 0.99 Hz); ^{183}W NMR (16.662 MHz, 0.8 M HCl/D_2O, $+LiClO_4$, $-CsClO_4$, 2.0 M Na_2WO_4 in D_2O standard): $\delta = -127.6$ (s, 24 W), -132.8 (s, 12 W); elemental analysis (%) calcd for $Cs_{20}[Nb_4O_6(Nb_3SiW_9O_{40})_4] \cdot 70\,H_2O$: H 0.95, Cs 18.0, Nb 10.1, W 44.7; found: H 1.01, Cs 18.4, Nb 9.82, W 44.2.

$Cs_{15}H_5$ salt (Cs-**1**): Concentration of a saturated solution of the Cs_{20} salt in 0.8 M HCl by evaporation in air over three days at 25 °C afforded colorless crystalline Cs-**1**. The FT-IR and ^{183}W NMR spectra of the Cs_{20} salt of **1** and Cs-**1** are identical. Elemental analysis (%) calcd for $Cs_{15}[H_5Nb_4O_6(Nb_3SiW_9O_{40})_4] \cdot 50\,H_2O$: H 0.77, Cs 14.5, Nb 10.8, W 48.1; found: H 0.76, Cs 14.5, Nb 10.7, W 48.0.

nBu_4N^+ salt ($TBA_{12}H_8$-**1**): $TBAHSO_4$ (5.75 g) dissolved in HCl (20 mL of a 0.8 M solution) was added to the Cs_{20} salt of **1** (1.5 g) in HCl (100 mL of a 0.8 M solution). The resulting white powder (yield = 99.6%) was recrystallized from CH_3CN using diethyl ether diffusion to provide 1.37 g of product. FT-IR (KBr pellet): $\tilde{\nu}$ [cm^{-1}]: 1005 (w), 967 (m), 915 (s), 800 (vs), 698 (s, Nb-O-Nb), 602 (w), 540 (vw); elemental analysis (%) calcd for $TBA_{12}H_8[Nb_4O_6(Nb_3SiW_9O_{40})_4]$: C 16.7, H 3.22, N 1.22, Nb 10.8, W 48.0; found: C 16.5, H 3.11, N 1.23, Nb 10.6, W 47.9.

Cyclic voltammograms of **1**, **2**, and **3** were recorded using a glassy carbon working electrode, a Pt wire counter electrode and a Ag/AgCl (3 M NaCl) reference electrode as Cs salts in aqueous $0.1\,\text{M}$ $NaClO_4$ under Ar at 24 °C with sweep rates of $100\,mV\,s^{-1}$. $HClO_4$ was used to adjust the pH.

Received: April 26, 1999 [Z13316IE]
German version: *Angew. Chem.* **1999**, *111*, 3413–3416

Keywords: cluster compounds • niobium • polyoxometalates • supramolecular chemistry • tungsten

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[13] Crystal data for $Cs_{14.9}H_{5.1}[Nb_4O_6(\alpha\text{-}Nb_3SiW_9O_{40})_4]\cdot 31\,H_2O$: Siemens SMART CCD diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Colorless block crystal, dimensions $0.38 \times 0.20 \times 0.15$ mm, monoclinic, space group $C2/c$ (No. 15); $a = 33.7982(1)$, $b = 30.2984(2)$, $c = 23.1300(1)$ Å, $\beta = 123.811(1)°$, $V = 20091.4(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 4.42\,g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 24.2\,mm^{-1}$, $F(000) = 23124$, $T = 293(2)$ K. A total of 17690 independent reflections, 13088 observed with $F_o > 4\sigma(F_o)$, $R_1 = 0.046$, $wR_2 = 0.139$, 1176 parameters. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on F^2 techniques with SHELXTL (v 5.03). Disorder in some of the cesium cations and water molecules was observed and partial occupancies were applied during the final stage of refinements. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-380219.

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[21] Solid-state FTIR spectra of Cs-**1**, nBu_4N-**1**, $Cs_8[Nb_6Si_2W_{18}O_{77}]$ (Cs-**3**), $(nBu_4N)_6[H_2Nb_6Si_2W_{18}O_{77}]$ (nBu_4N-**3**) exhibit broad peaks for the Nb-O-Nb stretch at 710, 698, 690, and 690 cm^{-1}, respectively. The M–O stretching region is very similar in all four samples consistent with maintenance of the Keggin structure in all four cases.

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Cerium(IV)-Catalyzed Deprotection of Acetals and Ketals under Mildly Basic Conditions[**]

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Dedicated to Professor Heinz G. Viehe on the occasion of his 70th birthday

The protection–deprotection sequence is probably the most frequently encountered functional-group transformation in organic synthesis.[1] Amongst the plethora of groups typically employed for protecting aldehydes and ketones, cyclic acetals and ketals enjoy a cardinal position, as exemplified by the numerous and ingenious methods devised for their attachment and removal.[2] Unfortunately, these protocols usually require harsh acidic conditions that are unsuitable for sensitive substrates.

A recently investigated example of this transformation is the deprotection of β-hydroxy ketal **1**[3] to give the corresponding highly acid-labile β-hydroxy ketone **2** (Table 1).[4] A variety of Brønsted and Lewis acids were ineffective and provided almost exclusively the α,β-unsaturated ketone **3**.

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[**] Financial support of this work was generously provided by the Université catholique de Louvain, Merck, the Actions de Recherche Concertées (convention 96/01–197), and the Fonds National de la Recherche Scientifique (Dossier N° 2.4571.98). I.E.M thanks the Fonds de la Recherche pour l'Industrie et l'Agriculture (FRIA) for providing studentships to B.L., A.A., and J.C.V. Rhodia and Zeneca are gratefully acknowledged for offering postdoctoral fellowships to A.G. and Y.Q., respectively. We are indebted to Prof. P. Claes and A. Masure for performing the cyclic voltammetric experiments and to Dr. H. G. Nedden for numerous improvements to the manuscript.