Synthesis, Characterization and Crystal Structure of the Water-Soluble, All-Inorganic Composition, A,β-Keggin Triniobium(V)-Substituted Polyoxotungstate

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Triniobium(V)-substituted β-Keggin polyoxotungstate, $K_7[A,\beta\text{-}SiW_9Nb_3O_{40}]\cdot 6H_2O$, as a soluble metal-oxide analogue and a metal-oxide support of the polyoxoanion-supported organometallic complexes, was synthesized, and the crystal and molecular structures of this polyoxoanion containing the Keggin A,β-SiW_9 unit were successfully determined for the first time.

Polyoxoanions are molecular metal-oxide clusters which resemble discrete fragments of solid metal-oxides.[1] The chemistry of triniobium(V)-substituted β-Keggin polyoxotungstate, $[\beta\text{-}SiW_9Nb_3O_{40}]^{7-}$, is interesting as an organic-solvent soluble metal-oxide analogue and also as a metal-oxide support of the polyoxoanion-supported organometallic complexes.[2] Recently, its application to epoxidation catalysis of olefins with hydrogen peroxide,[3a] antiviral activities in medicine,[4] and stabilizer of Rh^0 and Ir^0 nanoclusters[3b] has been also reported. However, organic-solvent soluble and water-insoluble forms such as all-Bu_4N salts or the mixed Bu_4N/Na salts are difficult to crystallize. In fact, crystal structure determination for this class of polyoxoanions has been limited only to Dawson-type polyoxotungstates, i.e. $Na(Bu_4N)_6[(Cp^*Rh)P_2W_{15}Nb_3O_{62}]\cdot 10MeCN\cdot 10Me_2CO$ ($Cp^* = C_5Me_5$)[5] and the unexpectedly formed $Na_9[\alpha\text{-}P_2W_{15}Nb_3O_{62}]\cdot 23H_2O\cdot 2MeCN$.[6]

We have so far reported the synthesis and isolation of the water-soluble, all-inorganic composition compounds, namely, alkali-metal salts of Dawson- and Keggin-type triniobium(V)-substituted polyoxotungstates, $[\alpha\text{-}P_2W_{15}Nb_3O_{62}]^{9-}$ [7a,c] and $[\beta\text{-}SiW_9Nb_3O_{40}]^{7-}$,[7e] and also the sodium salts of polyoxoanion-supported organometallic complexes $[(Cp^*Rh)P_2W_{15}Nb_3O_{62}]^{7-}$ [7b] and $[(Cp^*Rh)SiW_9Nb_3O_{40}]^{5-}$,[7d] all of which have been designed for crystallization. Since our report of synthesis and isolation of $L_7[A,\beta\text{-}SiW_9Nb_3O_{40}]$ (L = Li, Na, K and Cs) in 1998,[7e] considerable efforts have been made to get crystals suitable to X-ray analysis and solve the structure. In this work, we have determined the first X-ray structure of $K_7[A,\beta\text{-}SiW_9Nb_3O_{40}]$ as one of this series of compounds. Herein we report the synthesis, characterization, and crystal and molecular structures of $K_7[A,\beta\text{-}SiW_9Nb_3O_{40}]\cdot 6H_2O$ (**1**).

The water-soluble potassium salt **1** was derived from a stoichiometric reaction of the organic-solvent soluble, Nb–O–Nb bridged anhydride form $(Bu_4N)_6H_2[\beta,\beta\text{-}Si_2W_{18}Nb_6O_{77}]$[2c,8] with KBF_4 and subsequently with the required amount of KOH. The formation of **1** is shown in eq 1.

$$(Bu_4N)_6H_2[Si_2W_{18}Nb_6O_{77}] + 6\,KBF_4 + 8\,KOH \rightarrow 2\,K_7[SiW_9Nb_3O_{40}] + 6\,Bu_4NBF_4 + 5\,H_2O \quad (1)$$

Details of the preparation and isolation of **1** have been described elsewhere.[7e] Of four alkali-metal (Li, Na, K and Cs) salts of this polyoxoanion, the ease of crystallization found for **1** was remarkable. The composition and molecular formula of **1** were confirmed by complete elemental analysis, TG/DTA, positive-ion FABMS, FTIR, solution (^{183}W and ^{29}Si) NMR, and solid-state ^{29}Si NMR spectroscopy.[9] These data of compositional and spectroscopic characterization are consistent with the results of X-ray structure analysis.

X-ray structure analysis revealed the polyoxoanion depicted in Figure 1(b).[10] Selected bond lengths for the polyoxoanion are given in the caption of Figure 1. The crystals of **1** contained discrete cluster anions, potassium cations and lattice water molecules, all in general positions in the orthorhombic space group (*Pnma*). Three (K1, K2, K3) of the seven potassium cations were clearly identified in the crystal structure of compound **1**, but the others were disordered. The observed electron densities on the Nb and W atoms were quite different, and the data unequivocally distinguished and defined the Nb and W atoms. Five of the nine tungsten atoms, two of the three niobium atoms and one Si atom were clearly identified. The molecular structure of **1** was composed of the well-known Keggin-type $[\beta\text{-}SiW_{12}O_{40}]^{4-}$ structure with three Nb atoms substituting for the W atoms in the A-site (1,2,3-position, Figure 1(a)) consisting of three corner-linked WO_6 octahedra. Each of the three Nb atoms belonged to three different edge-shared NbW_2O_{13} groups (1, 4, 9-position etc., i.e. B-site) and each was linked to the others through the corner sharing (A-site). The fourth edge-shared W_3O_{13} group was rotated by 60° about the 3-fold axis from the α-isomer, which defines the β-isomer. Thus, the X-ray structure established that **1** contained a trisubstituted Keggin polyoxoanion with A,β-SiW_9 units. The three Nb atoms and nine W

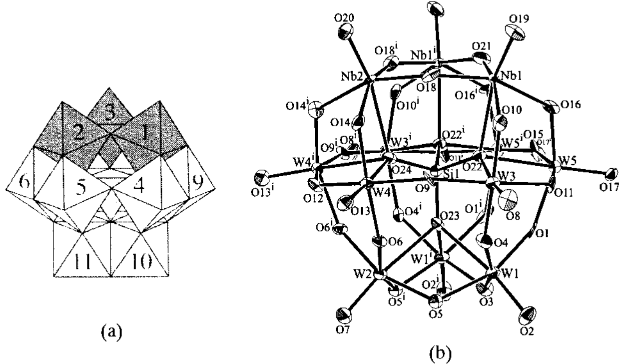

Figure 1. (a) Polyhedral representation of the $[A,\beta\text{-}SiW_9Nb_3O_{40}]^{7-}$ polyoxoanion, in which the three niobiums are represented by deep gray octahedra, the nine tungstens by white octahedra and one SiO_4 group by the central gray octahedron. (b) Molecular structure of **1** showing atoms with 50% thermal ellipsoids (symmetry operation; i; x, -0.5-y, z). Selected bond distances (Å): Nb1-O10 2.08(2), Nb1-O16 2.01(1), Nb1-O18 1.91(2), Nb1-O19 1.75(2), Nb1-O21 1.918(7), Nb1-O22 2.46(1), Nb2-O14 2.06(2), Nb2-O18 1.92(2), Nb2-O20 1.76(2), Nb2-O24 2.49(2), W1-O1 1.85(2), W1-O2 1.72(2), W1-O3 1.93(1), W1-O4 1.87(2), W1-O5 1.9335(9), W1-O23 2.35(2), W2-O5 1.9216(9), W2-O6 1.93(1), W2-O7 1.69(2), W2-O23 2.36(2).

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atoms all exhibited conventional octahedral coordination polyhedra. The W–Ot (Ot: terminal oxygen; 1.69(2)–1.72(2) Å) and Nb–Ot (1.75(2)–1.76(2) Å) distances were in the normal range. The cluster anion contained a central Si atom in an almost regular tetrahedral environment of SiO_4 with Si–O distances in the range of 1.63(2)–1.65(1) Å, and bond angles of 108(1)–110.2(7)°.

In comparison with the three corner-sharing octahedra (A-site) of the previously elucidated $K_4[\beta\text{-}SiW_{12}O_{40}]\cdot 9H_2O$,[11] the distances of Nb–Oe and Nb–Oa of **1** (2.01(1)–2.08(2) and 2.46(1)–2.49(2) Å, respectively; Oe: edge-sharing OM_2 oxygen; Oa: OM_3 oxygen linked to the central Si atom) are longer than those of W–Oe and W–Oa (1.72(7)–1.94(7) and 2.25(8)–2.40(8) Å, respectively), but the distance of Nb–Oc of **1** (Oc: corner-sharing OM_2 oxygen; 1.91(2)–1.918(7) Å) is shorter than that of W–Oc (1.93(3)–2.02(8) Å), while the Nb–Ot distance (1.75(2)–1.76(2) Å) of **1** is comparable to that of W–Ot (1.68(11)–1.83(68) Å). In the fourth edge-shared W_3O_{13} groups (B-site) of both β-Keggin polyoxoanions, the distances of W–Oe, W–Oa and W–Ot of **1** (1.9216(9)–1.9335(9), 2.35(2)–2.36(2) and 1.69(2)–1.72(2) Å, respectively) are shorter than those of $K_4[\beta\text{-}SiW_{12}O_{40}]$ (1.95(5)–1.99(7), 2.36(11)–2.53(16) and 1.75(6)–1.79(20) Å, respectively), while the distance of W–Oc of **1** (1.85(2)–1.93(1) Å) is comparable to that of $K_4[\beta\text{-}SiW_{12}O_{40}]$ (1.78(8)–2.00(11) Å). The octahedral radius of the niobium(V) atom (0.78 Å) is slightly larger than that of the tungsten(VI) atom (0.74 Å).[12a] Nevertheless, of particular note is the fact that the A-site unit of three corner-shared NbO_6 octahedra and the B-site unit of three edge-shared WO_6 octahedra of **1** are contracted, compared with those of $K_4[\beta\text{-}SiW_{12}O_{40}]$. The bond-valence sum (BVS)[12b,c] values were calculated from the observed bond lengths to be 5.19 and 5.05 for Nb1 and Nb2 atoms, respectively, and in the range of 5.93–6.27 for the W1–W5 atoms, and 3.84 for the central Si atom. As to the related Keggin polyoxoanions containing A,β-PW_9 unit, the X-ray structures for $(Me_4N)_3[PW_9Mo_3O_{40}]$,[13a] $Cs_{5.4}H_{0.6}[PW_9V_3O_{40}]$,[13b] and $Cs_6[PW_9(NbO_2)_3O_{37}]\cdot HCl\cdot 6.5H_2O$[13c] have been recently reported.

In summary, the water-soluble potassium salt of triniobium(V)-substituted A,β-Keggin polyoxotungstate **1** was isolated and the first X-ray structure analysis successfully performed. A difference of multicenter active sites (B-site vs A-site) in the Dawson and Keggin polyoxotungstates was revealed.

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8 The precursor $(Bu_4N)_6H_2[\beta,\beta\text{-}Si_2W_{18}Nb_6O_{77}]$ was prepared as previously described[2c] through syntheses of $Na_9H[A\text{-}\beta\text{-}SiW_9O_{34}]\cdot 23H_2O$, $K_7H[Nb_6O_{19}]\cdot 13H_2O$, $(Bu_4N)_{8-x}H_x[Si_2W_{18}Nb_6O_{77}]$ ($x \leqq 2$) and crude $(Bu_4N)_6H_2[Si_2W_{18}Nb_6O_{77}]$, and recrystallization from MeCN.

9 Compound **1**, prepared as previously described,[7e] was readily crystallized as colorless needles within a week with vapor diffusion from 25 mL acetone into the aqueous solution of 0.2 g of the sample dissolved in 3.0 mL of pH 8 unbuffered solution. The crystals obtained in 0.17 g (85%) yield were hygroscopic, very soluble in water and soluble in DMSO, but insoluble in most organic solvents. Anal. Found: H, 0.12; K, 9.43 Si, 1.06; W, 57.4; Nb, 9.65; O, 23.3%. Calcd for $H_2K_7SiW_9Nb_3O_{41}$ or $K_7[SiW_9Nb_3O_{40}]\cdot H_2O$: H, 0.07; K, 9.43; Si, 0.97; W, 57.2; Nb, 9.63; O, 22.7%. A weight loss of 3.54% (weakly solvated or adsorbed water) was observed during overnight drying at room temperature under reduced pressure (10^{-3}–10^{-4} Torr) before the analysis. TG/DTA under atmospheric conditions: a weight loss of 3.38% was observed below 500 °C, with a clear endothermic peak at 91 °C; calcd 3.62% for x = 6 in $K_7[SiW_9Nb_3O_{40}]\cdot xH_2O$. A positive-ion FABMS: a molecular ion peak, $[M + H]^+ = m/z$ 2875.8 was observed for $K_7SiW_9Nb_3O_{40}$. FTIR (KBr disk) in the polyoxometalate region: 993m, 954s, 883s, 794s, 539m, 474w cm^{-1}. ^{183}W NMR (D_2O, 24.5 °C): δ –118.0 (6W, $\Delta\nu_{1/2}$ = 1.7 Hz); –124.9 (3W, $\Delta\nu_{1/2}$ = 1.8 Hz). ^{29}Si NMR (D_2O, 27.0 °C): δ –82.8. Solid-state ^{29}Si NMR (CP/MAS 80 Hz, 25.0 °C): δ –81.5.

10 A colorless needle crystal (0.20 × 0.10 × 0.10 mm) was sealed in a glass capillary. The reflection data were collected on a Rigaku AFC5S four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at room temperature. Data were corrected for Lorentz and polarization effects. The X-ray data were also corrected for absorption. The structure was solved by direct methods followed by subsequent difference Fourier calculation and refined by a full-matrix least-squares procedure using TEXSAN package.[14] One oxygen atom (O5) was refined isotropically, but all other non-hydrogen atoms were refined anisotropically. Crystal data for $H_{12}K_7SiW_9Nb_3O_{46}$, M_r = 2983.21, orthorhombic, space group *Pnma* (# 62), a = 24.662(3), b = 15.927(2), c = 12.403(2) Å, V = 4872(1) Å^3, Z = 4, D_c = 4.067 g cm^{-1}, μ(Mo Kα) = 225.85 cm^{-1}. Final R = 0.057, R_w = 0.078, and GOF = 1.50 (6192 total reflections, 6192 unique reflections of which 3959 with $I > 2.00\sigma(I)$ were used in all calculations).

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