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Synthesis and Structure of Dilacunary Decatungstogermanate, [γ-$GeW_{10}O_{36}$]$^{8-}$

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The dilacunary decatungstogermanate [γ-$GeW_{10}O_{36}$]$^{8-}$ (**1**) has been synthesized and structurally characterized in solution and in the solid state. Reaction of germanium dioxide with sodium tungstate in aqueous acidic medium results in the formation of [β_2-$GeW_{11}O_{39}$]$^{8-}$ (**2**), which is then used as a precursor for the synthesis of **1**. The ^{183}W spectrum of **2** shows the expected 11 peaks of equal intensity, whereas that of **1** exhibits the expected three peaks with relative intensities 2:2:1. Polyanion **1** represents a novel lacunary polyoxometalate, giving rise to a multitude of derivatives by reaction with transition metals, lanthanides, and other electrophiles.

The chemistry of polyoxometalates (POMs) is a rapidly growing field because these nanomolecular entities exhibit a unique combination of tunable properties, including composition, size, shape, charge density, redox potentials, and solubility.[1] The main goal in the synthesis of POMs is usually the discovery of novel species with unexpected structures and properties. This is mostly accomplished by incorporation of functional units, which can be transition metals, lanthanides, organometallic entities, etc. POMs possess interesting properties that can be manifested in many applications, e.g., catalysis, biochemical separation, medicinal chemistry, magnetism, and materials science.[2]

Silicotungstates represent a well-known subclass of POMs, and to date a number of plenary, as well as lacunary, derivatives are known.[3] In 1986, Hervé and co-workers reported the dilacunary Keggin derivative [γ-$SiW_{10}O_{36}$]$^{8-}$.[4] Since then, this polyanion has become a popular precursor for several groups.[5] The decatungstosilicate itself, as well as some of its transition metal derivatives, has shown interesting catalytic properties.[6]

Hervé and Tézé were also able to prepare germanium analogues for some of the known lacunary silicotungstates. To date, [α-GeW_9O_{34}]$^{10-}$, [β-$HGeW_9O_{34}$]$^{9-}$, [α-$GeW_{11}O_{39}$]$^{8-}$, and [β_x-$GeW_{11}O_{39}$]$^{8-}$ ($x = 1, 2, 3$) have been synthesized and characterized by polarography, elemental analysis, UV, and IR spectroscopy.[7]

Here we report on the synthesis and structural characterization of the dilacunary [γ-$GeW_{10}O_{36}$]$^{8-}$ (**1**) and its monolacunary precursor [β_2-$GeW_{11}O_{39}$]$^{8-}$ (**2**).

The synthesis procedures for **2**[8] (isolated as K_8[β_2-$GeW_{11}O_{39}$]·14H_2O, **K-2**) and **1**[9] (isolated as K_8[γ-$GeW_{10}O_{36}$]·6H_2O, **K-1**) closely follow those of Tézé and Hervé for the silicon analogues.[3,7] The main difference is that we replaced sodium metasilicate by germanium dioxide. We did not obtain single-crystal X-ray data for **2**, but ^{183}W NMR in solution resulted in the expected 11 peaks at −72.6, −81.1, −85.4, −91.7, −97.3, −108.8, −120.7, −125.9, −143.3, −163.8, and −180.0 ppm (see Figure 1). This is fully

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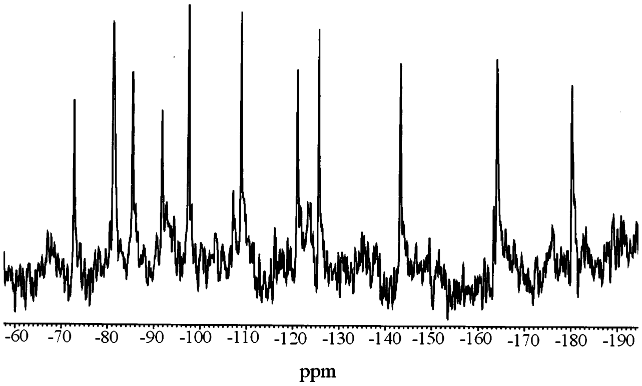

Figure 1. ^{183}W NMR spectrum of **K-2** in D_2O at 293 K.

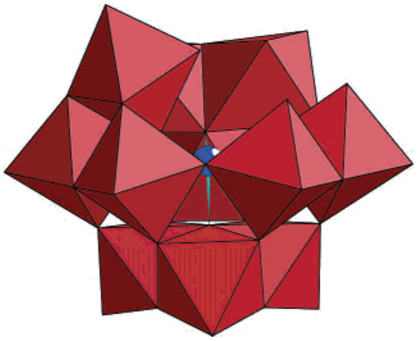

Figure 2. Suggested structure of **2** (Ge, blue; WO_6, red).

consistent with the formula $[\beta_2\text{-GeW}_{11}O_{39}]^{8-}$ which represents a chiral Keggin structure with the vacancy being situated in the belt adjacent to the rotated triad (see Figure 2).

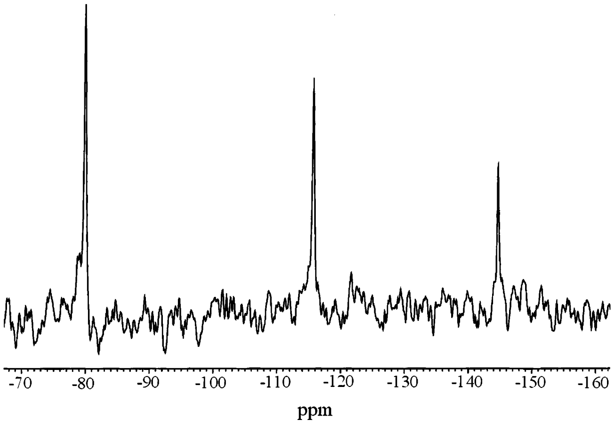

Figure 3. ^{183}W NMR spectrum of **K-1** in D_2O at 293 K.

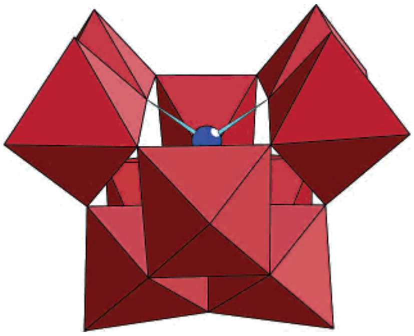

Figure 4. Combined polyhedral/ball-and-stick representation of **1** (Ge, blue; WO_6, red).

Polyanion **1** was synthesized from **2** in a short one-pot procedure, essentially analogous to that reported by Hervé for the Si derivative.[3,4] However, we discovered that the yield of **1** was significantly higher (92% vs 42%) when we worked at pH 8.8 instead of 9.1.[9,10] Solution ^{183}W NMR of **1** resulted in the expected three peaks at −80.0, −115.9, and −144.9 ppm with relative intensities 2:2:1 (see Figure 3). These signals are all shifted downfield (∼15−20 ppm) compared to those of $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ (−96.4, −137.2, and −158.2 ppm).[3,4] Single-crystal X-ray analysis[11] on **1** revealed that it is indeed the Ge analogue of $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$, see Figure 4.

The main differences between **1** and $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ are the respective heteroatom−oxygen bond lengths, which are longer and much more similar in the former (1.72, 1.74, 1.76, 1.77(2) Å) than in the latter (1.54, 1.59, 1.68, 1.68(5) Å). As expected, the W−O(Ge) bonds are on average somewhat shorter (2.25(2) Å) than the W−O(Si) bonds (2.29(4) Å). For the remaining tungsten−oxo distances, there are no significant differences between **1** and $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$. The bond valence sums[12] (bvs) for the four terminal oxygens O4A, O5A, O9A, and O10A at the lacunary site of **1** (bvs = 1.58, 1.46, 1.49, and 1.58, average bvs = 1.53) are somewhat smaller than those for the other terminal oxo groups of **1** (bvs = 1.58−1.98, average bvs = 1.72). In analogy with $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ and when considering the pH of synthesis (8.8), we assume that **1** is not protonated at these conditions.[3,4] Nevertheless, we expect that **1** becomes pro-

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(8) Preparation of β_2-undecatungstogermanate, $K_8[\beta_2\text{-GeW}_{11}O_{39}]\cdot 14H_2O$ (**K-2**). Germanium dioxide (5.4 g, 0.052 mol) was dissolved in 100 mL of water (solution A). Then, 182 g of sodium tungstate (0.552 mol) was dissolved in 300 mL of water in a separate beaker (solution B). To this solution, 165 mL of 4 M HCl was added with vigorous stirring in small portions over 15 min. Then, solution A was poured into the tungstate solution (solution B), and the pH adjusted to between 5.2 and 5.8 by addition of 4 M HCl solution (∼40 mL). This pH was maintained for 100 min by addition of the HCl solution. Then, 90 g of solid KCl was added with gentle stirring. After 15 min, the precipitate (yield: 112.1 g, 68%) was collected by filtration on a sintered glass filter. IR for **K-2**: 946(s), 872(sh), 840(s), 811(s), 777(sh), 719(s), 618(w), 521(m), 473(m), 437 (m) cm^{-1}. Anal. Calcd (Found) for **K-2**: K 9.5 (9.1), W 61.6 (61.8), Ge 2.2 (2.0). ^{183}W NMR (D_2O, 293 K) for **2**: −72.6, −81.1, −85.4, −91.7, −97.3, −108.8, −120.7, −125.9, −143.3, −163.8, −180.0 ppm (all equal intensity).

(9) Preparation of γ-decatungstogermanate, $K_8[\gamma\text{-GeW}_{10}O_{36}]\cdot 6H_2O$ (**K-1**). **K-2** (15.2 g, 4.63 mmol) was dissolved in 150 mL of water. A small amount of insoluble material was removed by rapid filtration on a fine frit or through Celite. The pH of the solution was quickly adjusted to 8.7−8.9 by addition of a 2 M aqueous solution of K_2CO_3. The pH was kept at this value by addition of the K_2CO_3 solution for exactly 16 min. The product was then precipitated by addition of solid KCl (40 g). During the precipitation (10 min), the pH was maintained at 8.8 by addition of small amounts of the K_2CO_3 solution or dilute HCl as needed. Then, the solid (yield: 12.4 g, 92%) was filtered off and air-dried. IR for **K-1**: 936(m), 889(sh), 827(s), 805(s), 727(s), 531(m), 478(m), 419 (w) cm^{-1}. Anal. Calcd (Found) for **K-1**: K 10.8 (10.2), W 63.2 (63.2), Ge 2.5 (2.2). ^{183}W NMR (D_2O, 293 K) for **1**: −80.0, −115.9, −144.9 ppm (relative intensities 2:2:1).

(10) We discovered that the yield of $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ can also be improved from 42% to 60% by working at pH 8.8.

(11) Polyanion **1** was crystallized as a mixed cesium−potassium salt by layering a solution of **K-1** with a few drops of 1 M CsCl and slow evaporation of the solvent. Crystal data for **CsK-1**: $Cs_7K[\gamma\text{-GeW}_{10}O_{36}]\cdot 6H_2O$, $M = 3564.7$, monoclinic, space group $P2_1$, $a = 9.7823(6)$ Å, $b = 19.4732(14)$ Å, $c = 12.2177(10)$ Å, $\beta = 92.099(5)°$, $V = 2325.8(3)$ Å^3, $Z = 2$, $T = 24$ °C, $D_{\text{calc}} = 4.923$ mg/m^3, abs. coeff. = 30.274 mm^{-1}, $\lambda = 0.71073$ Å, $R\ [I > 2\sigma(I)] = 0.0667$, R_w (all data) = 0.1821, Flack parameter = −0.01(2).

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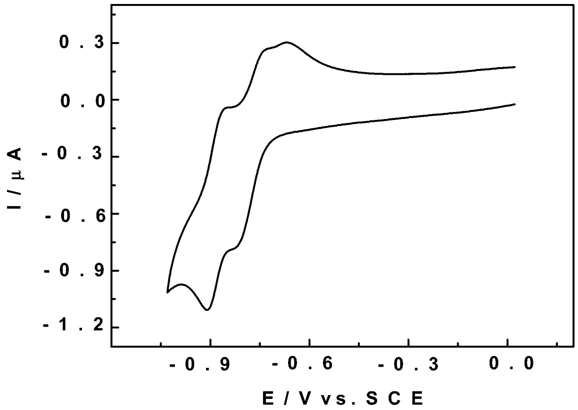

Figure 5. Cyclic voltammogram of 2×10^{-4} M **K-1** run in a pH 5 (1 M $CH_3COONa + CH_3COOH$) buffer solution. The scan rate was 2 mV/s, the working electrode was glassy carbon, and the reference electrode was SCE. The glassy carbon (3 mm diameter) handling, and the electrochemical setup were described previously.[14]

tonated in more acidic media and we suggest that this occurs first at the most basic oxygens O4A, O5A, O9A, and O10A. Currently, there is a dispute on the tetraprotonated form of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ regarding mono- or diprotonation of these four oxygens.[6b,13] It remains to be seen how **1** behaves in this respect.

In addition to **1** and $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$, the same dilacunary γ-Keggin polyanion structure is also known with P as the heteroatom in $[\gamma\text{-}PW_{10}O_{36}]^{7-}$.[3] In principle, it should also be possible to prepare the hypothetical As derivative $[\gamma\text{-}AsW_{10}O_{36}]^{7-}$.

The cyclic voltammogram of **1** at pH 5 (1 M $CH_3COONa + CH_3COOH$), is represented essentially by two reduction waves located at −0.825 and −0.909 V vs SCE, respectively (see Figure 5), in complete agreement with the pattern described for $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$.[3,4] The two waves are chemically reversible; however, the reoxidation wave associated with the first reduction process is composite. At a slow scan rate, splitting of this reoxidation pattern into two waves is observed (see Figure 5). The same observation was made with the analogous species $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ under the same experimental conditions. Controlled potential coulometry performed on the first wave at −0.825 V vs SCE shows a consumption of two electrons per molecule.

In summary, we have synthesized and structurally characterized the novel dilacunary decatungstogermanate **1** in solution (^{183}W NMR, electrochemistry) and in the solid state (XRD, FTIR). Furthermore, we report on the ^{183}W NMR of the monolacunary undecatungstogermanate **2**. Polyanion **1** is isostructural with its Si analogue $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$. Therefore, we expect **1** to exhibit similar reactivity, in particular when reacted with transition metal ions, rare earths, organometallic groups, and other electrophiles. In fact, we have already isolated several transition metal (e.g., Fe, Mn, Co, Cu, Ru)-substituted derivatives of **1** which will be published elsewhere. Considering the highly interesting catalytic activity of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ in the oxidation of olefins with H_2O_2,[6b] we are interested if **1** behaves similarly. Furthermore, we will test **1** and **2**, as well as their functionalized derivatives, in other catalytic reactions using different substrates and oxidants. Finally, SQUID and EPR measurements will be performed on magnetic derivatives of **1** and **2**.

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Supporting Information Available: X-ray crystallographic data for **CsK-1** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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