$F \geq 2.0\sigma(F_o)$. The intensity data were collected on a Bruker CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation at room temperature. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-141837 for **1** and -141836 for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Controlled Assembly of Polyoxometalate Chains from Lacunary Building Blocks and Lanthanide-Cation Linkers**

Masahiro Sadakane, Michael H. Dickman, and Michael T. Pope*

Polyoxometalates, in addition to their considerable potential as catalysts and catalytic precursors, and their applications in biochemistry and medicine,[1] are attracting increased attention as components of supramolecular complexes and materials.[2]

In recent years, a number of very large polyoxometalate anions have been synthesized and structurally characterized. Beginning with the "big wheel" Mo_{154} anion, Müller's group have reported several giant mixed-valence polyoxomolybdates with cyclic (Mo_{176}),[3] icosahedral (Mo_{132}),[4] capped cyclic (Mo_{248}),[5] and "basket" (Mo_{116})[6] architectures. In polytungstate chemistry we have described quite different structures (for example W_{148}),[7] and Zubieta and co-workers have reported one- and two-dimensional polymeric oxometalates in several organic-inorganic hybrid materials.[8] Although these substances and materials can be synthesized in modest to good yield from monometallic components in one-pot reactions, it is of course generally true that the composition and structure of the products could not have been predicted. However, once structural principles are recognized, syntheses of targeted species can be designed, as has been demonstrated by the work of Müller and co-workers with the large polymolybdates.

In the course of our investigations into the construction of large inorganic clusters from lacunary polyoxotungstate anions with lanthanide (Ln) or actinide cations as assembling groups,[9] we report a new simple strategy to yield infinite one-dimensional polyxoxometalates that are recrystallizable from aqueous solution. Two types of polymer chain are exemplified in the structures of the ammonium salts of **1** and **2**. These are 1:1 complexesof the type first reported by Peacock and

$[Ce(\alpha\text{-}SiW_{11}O_{39})(H_2O)_3]^{5-}$ **1**

$[La(\alpha\text{-}SiW_{11}O_{39})(H_2O)_3]^{5-}$ **2**

Weakley,[10] and they can be isolated by mixing solutions of the lacunary polytungstates with approximately 3.8 equivalents of $Ln(NO_3)_3$, and recrystallization from aqueous ammonium chloride. The excess $Ln(NO_3)_3$ ensures high yields of the desired product. Decreasing the amount of $Ln(NO_3)_3$ results in the formation of the 1:2 complex ($[Ln(\alpha\text{-}SiW_{11}O_{39})_2]^{13-}$) as a side product. If present, this 1:2 complex can be removed by recrystallization.

As shown in Figures 1 and 2, the anions are polymeric in the solid state. The $\alpha\text{-}SiW_{11}O_{39}$ units are connected by the

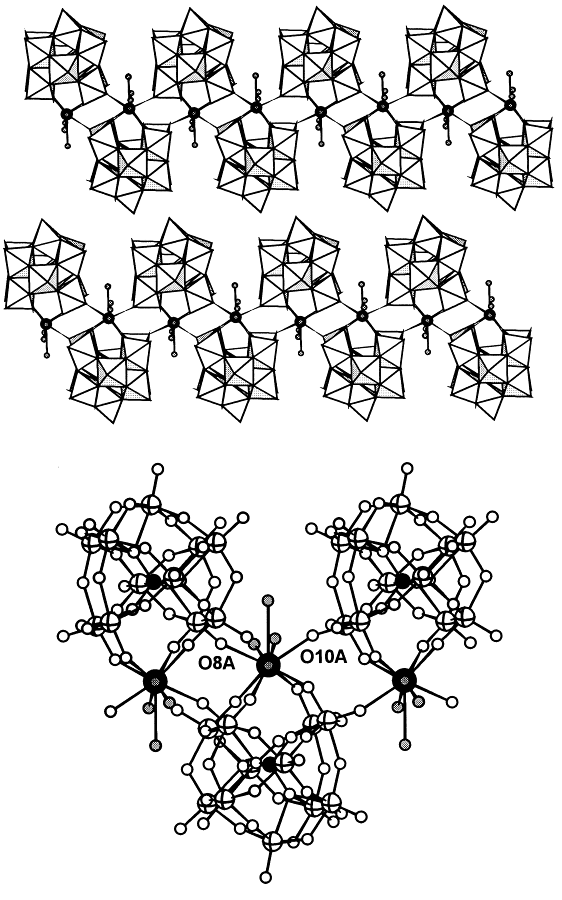

Figure 1. Structure of **1** Top: Polyhedral representation (black circle: cerium and gray circle: water oxygen). Bottom: Ball-and-stick representation (large black circle: cerium, small black circle: silicon, open circle: oxygen, gray circle: water oxygen, and crossed circle: tungsten). The chain is parallel to the crystallographic *a* axis.

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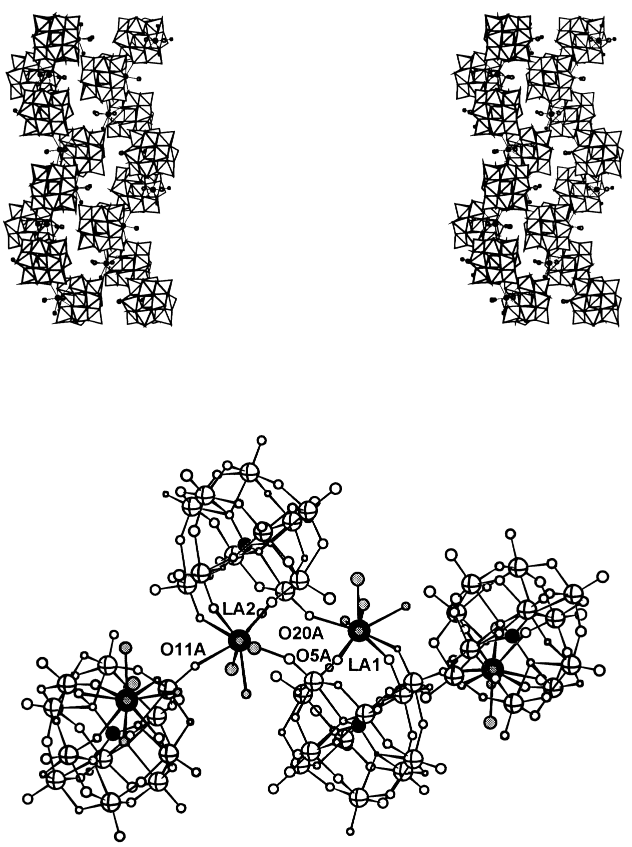

Figure 2. Structure of **2** Top: Stereoview of the polyhedral representation. Bottom: Ball-and-stick representation (large black circle: lanthanum, small black circle: silicon, open circle: oxygen, gray circle: water oxygen, and crossed circle: tungsten).

lanthanide cations, and the structure of the polymer depends on the identity of the connecting cation. The cerium complex **1** is a polymer with an inversion center between the two $[Ce(\alpha\text{-}SiW_{11}O_{39})(H_2O)_3]^{5-}$ units in the unit cell (Figure 1), and the lanthanum complex **2** is a polymer with no inversion center (Figure 2). Both lanthanide cations are coordinated by nine oxygen atoms in a distorted monocapped square-antiprism environment. The four oxygen atoms that form one uncapped face are the oxygen atoms that surround the vacant site of the lacunary anion. In **1** the cerium cations are additionally coordinated by two neighboring $\alpha\text{-}SiW_{11}O_{39}$ units, through terminal oxygen atoms (O8A and O10A), and by three water oxygen atoms (gray circles, Figure 1). In the lanthanum complex **2**, on the other hand, two kinds of lanthanum atoms(LA1 and LA2 in Figure 2) alternate in the chain; LA1 is coordinated by only one additional $\alpha\text{-}SiW_{11}O_{39}$ unit through O20A, while LA2 is coordinated by two additional $\alpha\text{-}SiW_{11}O_{39}$ units through O5A and O11A. The average bond length between the lanthanide cation and oxygen atom (2.54(17) Å for **1** and 2.56(5) Å for **2**) is comparable to the sum of the Ln–O ionic radii for 9-coordinate Ln^{3+} and 2-coordinate O^{2-} ions (2.546 Å for Ce–O and 2.566 Å for La–O).[11] The larger standard deviation for the average Ce–O bond length is a consequence of the longer "capping water" distance (2.98(4) Å) compared with the corresponding La–O bond lengths (2.69(2) and 2.58(2) Å). The interatomic distances between the lanthanide centers are 6.554 and 6.596 Å for **1**; 6.880 and 7.644 Å for **2**.

The poly-$[Ce(\alpha\text{-}SiW_{11}O_{39})(H_2O)_3]$ anion chains in **1** are arranged parallel to the crystallographic *a* axis (Figure 3, upper), whereas the bulkier poly-$[La(\alpha\text{-}SiW_{11}O_{39})(H_2O)_3]$ anion chains in **2** mesh together in both the *ac* and *ab* planes (Figures 2 and 3).

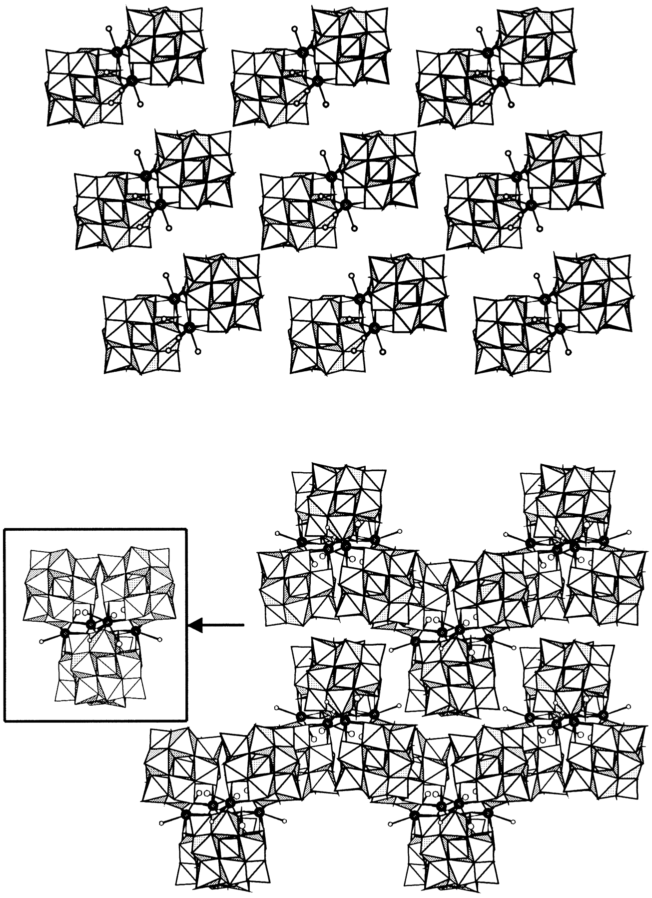

Figure 3. Packing of anions in planes perpendicular to chain axis. Top: **1** viewed down the crystallographic *a* axis. Bottom: **2** viewed down the crystallographic *c* axis. The *a* axis is horizontal. The inset shows a view down a single anion chain of **2**.

Although **1** and **2** exist in polymeric form in the solid state, there is good evidence to show that in aqueous solution they dissociate into the monomeric building blocks, $[Ln(\alpha\text{-}SiW_{11}O_{39})(H_2O)_n]^{5-}$. The ^{183}W NMR spectra summarized in Table 1 show the characteristic six-line pattern consistent with the C_s symmetry of the $\alpha\text{-}SiW_{11}O_{39}$ group.[12] The differences in the chemical shifts observed in the spectra of solutions of **1**, **2**, the free $\alpha\text{-}SiW_{11}O_{39}$ anion, and the previously established 1:2 complexes[12c, 13] $[Ln(\alpha\text{-}SiW_{11}O_{39})_2]^{13-}$ demonstrate the identity and integrity of each species in solution.

Experimental Section

Crystals of the ammonium salts of **1** and **2** were isolated as follows: A hot (80 °C) solution of $K_8SiW_{11}O_{39} \cdot xH_2O$ (2.28 g, ca. 0.76 mmol) in water (10 mL) was added slowly to a hot (80 °C) stirred solution of $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Ce: 1.26 g, 2.90 mmol or La: 1.21 g, 2.79 mmol) in water (10 mL), over 30 min. After the solution had been stirred at this temper-

Table 1. ^{183}W NMR chemical shifts.

Complex	Chemical shift [ppm]
1[a]	326.3, 110.0, – 104.8, – 115.1, – 132.4, – 161.8
2[b]	– 110.5, – 117.3, – 139.7, – 144.8, – 171.5, – 173.7
$[\alpha-SiW_{11}O_{39}]^{8-}$[c]	– 105.2, – 106.0, – 120.5, – 121.6, – 143.5, – 173.5
$[Ce(\alpha\text{-}SiW_{11}O_{39})_2]^{13-}$[d]	313.6, 139.0, – 101.3, – 116.2, – 130.1, – 163.4
$[La(\alpha\text{-}SiW_{11}O_{39})_2]^{13-}$[e]	– 107.2, – 117.7, – 132.7, – 137.7, – 159.6, – 172.0

[a] Ammonium salt (0.3 g) in D_2O (2.5 mL). [b] Lithium salts were prepared in situ, because of the low solubility of the ammonium salt in D_2O. Lithium salt of $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ (1.5 g) in D_2O (5.0 mL) + 1 equiv of $La(NO_3)_3$. [c] Lithium salt of $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ (1.5 g) in D_2O (5.0 mL). [d] Ammonium salt (1.0 g) in D_2O (2.5 mL). [e] Lithium salt of $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ (1.5 g) in D_2O (5.0 mL) + 0.5 equiv of $La(NO_3)_3$.

ature for 5 min, a solution of 4 M NH_4Cl (30 mL) at the same temperature was added the reaction mixture allowed to cool to room temperature and filtered. Addition of a threefold excess of ethanol to the cooled filtrate yielded a precipitate (for **1** 1.84 g, 84.5 %; for **2** 1.97 g, 84.2 % based on $[SiW_{11}O_{39}]^{8-}$), which was collected by filtration and recrystallized twice from hot 2 M NH_4Cl solution to give 1.03 g (**1**) and 1.14 g (**2**) corresponding to yields of about 48 %.

Elemental analysis (KANTI Technologies, Inc., Amherst, NY, USA) of air-dried materials calcd % for $(NH_4)_5[Ce(SiW_{11}O_{39})] \cdot 7H_2O \cdot (NH_4Cl)_{0.5}$ (**1**): N 2.52, H 1.19, Ce 4.58, Si 0.92, W 66.15, Cl 0.57; found: N 2.41, H 1.32, Ce 4.06, Si 0.75, W 66.66, Cl 0.64; calcd % for $(NH_4)_5[La(SiW_{11}O_{39})] \cdot 5H_2O \cdot KCl$ (**2**): N 2.30, H 0.99, La 4.53, Si 0.92, W 65.90, K 1.27, Cl 1.16; found: N 2.32, H 1.10, La 4.51, Si 0.87, W 65.90, K 1.20, Cl 1.19; IR (KBr disk) in metal–oxygen stretching region: for **1**: $\tilde{\nu} = 1003$ (m), 954 (s), 895 (vs), 830 (s), 797 (s) cm^{-1}, and for **2**: $\tilde{\nu} = 1006$ (m), 947 (s), 891 (vs), 833 (s), 794 (s) cm^{-1}.

Crystal structure analysis: for **1** (orange block), $(NH_4)_5[Ce(SiW_{11}O_{39})] \cdot 11H_2O$, (although chloride ions in **1**, and potassium and chloride ions in **2** were found in the elemental analyses, these elements were not found in the crystal structures, this is either because of disorder or differences between the crystal and bulk sample. Less water was found in the elemental analyses than the crystal structures, because the bulk samples were air-dried), crystal dimension $0.30 \times 0.12 \times 0.05$ mm, crystal system triclinic, space group $P\bar{1}$, $a = 11.7451(1)$, $b = 12.3956(1)$, $c = 18.2487(2)$ Å, $\alpha = 76.78$, $\beta = 80.990(1)$, $\gamma = 86.291(1)°$, $V = 2554.70(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 4.034$ Mg m^{-3}, $2\theta_{max} = 56.64°$, total measured reflections 15454, independent reflections 11152, $R_{int} = 0.0850$, $\mu = 25.659$ mm^{-1}, analytical absorption correction, min./max. transmission 0.0332/0.3811, $R_1 = 0.0929$ for 8076 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.3084$ for all reflections, 354 parameters, highest residual electron density 8.980 e Å^{-3}; and for **2** (colorless block), formula $[(NH_4)_5\{La(SiW_{11}O_{39})\} \cdot 10H_2O]_2$, crystal dimension $0.16 \times 0.16 \times 0.20$ mm, crystal system orthorhombic, space group $Pca2_1$, $a = 22.7517(1)$, $b = 17.3293(2)$, $c = 24.3516(2)$ Å, $V = 9601.13(14)$ Å^3, $Z = 4$, $\rho_{calcd} = 4.267$ Mg m^{-3}, $2\theta_{max} = 56.52°$, total measured reflections 103602, independent reflections 23092, $R_{int} = 0.1200$, empirical absorption correction based on measured intensities of equivalent reflections at different phi and omega values ($\mu = 27.249$ mm^{-1}, min./max. transmission 0.0377/0.0963),[14] $R_1 = 0.0694$ for 18276 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.1650$ for all reflections, 690 parameters, highest residual electron density 9.413 e Å^{-3}.

Single-crystal X-ray analyses were performed on a Bruker–Siemens SMART CCD single-crystal diffractometer equipped with a Mo anode and graphite monochromator (Kα wavelength = 0.71073 Å). An approximate sphere of data was collected using ω scans. Crystals were mounted on a glass fiber under mineral oil to prevent water loss, and placed in a nitrogen stream at 173(2) K. Routine Lorentz-polarization corrections were applied. All structures were solved using direct methods and refined against F^2 over all independent reflections using the routines included in the SHELXTL-PC software suite.[15] No hydrogen atoms were included. Nitrogen atoms of ammonium cations were modeled as oxygen atoms because nitrogen atoms could not be distinguished from oxygen atoms. Bond valence sum calculations[16] did not clearly indicate any protonated oxygen atoms in the anion other than the water coordinated to lanthanide ions. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-411198 (**1**) and CDD-411199 (**2**).

^{183}W NMR was recorded at 12.504 MHz on a Bruker AM 300WB spectrometer with 2 M Na_2WO_4 as an external standard at room temperature.

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