

Solid-State and Solution Studies of $\{\text{Ln}_n(\text{SiW}_{11}\text{O}_{39})\}$ Polyoxoanions: An Example of Building Block Condensation Dependent on the Nature of the Rare Earth

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The reactivity of the $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ monovacant polyoxometalate with lanthanide has been investigated for four different trivalent rare-earth cations ($\text{Ln} = \text{Nd}^{\text{III}}, \text{Eu}^{\text{III}}, \text{Gd}^{\text{III}}, \text{Yb}^{\text{III}}$). The crystal structures of $\text{KCs}_4[\text{Yb}(\alpha\text{-SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_2] \cdot 24\text{H}_2\text{O}$ (**1**), $\text{K}_{0.5}\text{Nd}_{0.5}[\text{Nd}_2(\alpha\text{-SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_{11}] \cdot 17\text{H}_2\text{O}$ (**2a**), and $\text{Na}_{0.5}\text{Cs}_{4.5}[\text{Eu}(\alpha\text{-SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_2] \cdot 23\text{H}_2\text{O}$ (**3a**) are reported. The solid-state structure of compound **1** consists of linear wires built up of $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ anions connected by Yb^{3+} cations, while the linkage of the building blocks by Eu^{3+} centers in **3a** leads to the formation of zigzag chains. In **2a**, dimeric $[\text{Nd}_2(\alpha\text{-SiW}_{11}\text{O}_{39})_2(\text{H}_2\text{O})_8]^{10-}$ entities are linked by four Nd^{3+} cations. The resulting chains are connected by lanthanide ions, leading to a bidimensional arrangement. Thus, the dimensionality, the organization of the polyoxometalate building units, and the $\text{Ln}/[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ ratio in the solid state can be tuned by choosing the appropriate lanthanide. The luminescent properties of compound **3a** have been studied, showing that, in solution, the polymer decomposes to give the monomeric complex $[\text{Eu}(\alpha\text{-SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_4]^{5-}$. The lability of the four exogenous ligands connected to the rare earth must allow the functionalization of this lanthanide polyanion.

Introduction

Heteropolyacids (HPAs) are an important class of compounds which are mainly obtained by acidobasic condensation of vanadium, molybdenum, or tungsten in the presence of a heteroatom.¹ They are used in fields as diverse as analytical chemistry, oxidation catalysis, medicine, or magnetochemistry.² Polyoxometalate (POM) clusters are generally reported as discrete entities, and it is only recently that the considerable development of synthesis in hydrothermal conditions allowed the characterization of multidimensional

POM assemblies. Nevertheless, it remains a challenge to control the aggregation process occurring when this synthetic approach is used. In low temperature and pressure conditions, few compounds containing polymers built up by linking POMs with transition-metal³ or lanthanide⁴ centers have been obtained, and the design of such systems remains largely to explore. The behavior of silicotungstates in solution has been widely studied and the monovacant, divacant, and trivacant derivatives of the $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ Keggin anion characterized.⁵ Among the four identified isomers of the $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ monovacant complex, only the $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ species has

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been found to be stable in solution. Peacock and Weakley studied the interaction between this isomer and lanthanide cations.⁶ They reported that $[\alpha-SiW_{11}O_{39}]^{8-}$ forms both 1:1 and 1:2 compounds with rare earths. The 1:2 complexes $\{Ln(SiW_{11}O_{39})_2\}$ were isolated, and Blasse et al.⁷ postulated, by analogy with the known structure of $Cs_{12}[U(GeW_{11}O_{39})_2]$ obtained by Tourné et al.,⁸ that two POMs encapsulate an eight-coordinated lanthanide. The luminescence properties of the relative Eu^{III} complex were studied, and confirmed that no water molecule was coordinated to the lanthanide.⁹ Finally, in 2000, Pope et al. reported the structural characterization of the monodimensional 1:1 $[Ln(\alpha-SiW_{11}O_{39})(H_2O)_3]^{5-}$ ($Ln = La^{III}, Ce^{III}$) compounds, showing that these anions are polymeric in the solid state.¹⁰ Interestingly, even if the structures of the cerium and the lanthanum compounds were closely related, Pope et al. noticed that some differences exist; e.g., an inversion center is present between the two $[Ce(\alpha-SiW_{11}O_{39})(H_2O)_3]^{5-}$ units in the unit cell, whereas the lanthanum complex is a polymer without an inversion center. We report here that the solid-state structures of the $Ln/[\alpha-SiW_{11}O_{39}]^{8-}$ compounds are strongly dependent on the lanthanide used, and therefore represent a rare example where the nature of the rare earth imposes the arrangement of the building units and the stoichiometric Ln/POM ratio. The photophysical characterization of the europium compound in the solid state and in solution is also reported, and confirms that the polymer decomposes in water to generate the monomeric $[Eu(\alpha-SiW_{11}O_{39})(H_2O)_4]^{5-}$ complex.

Experimental Section

Chemicals and Reagents. All chemicals were used as purchased without purification. $K_8[SiW_{11}O_{39}] \cdot 13H_2O$ was synthesized as previously described.⁵

Synthesis of $KCs_4[Yb(\alpha-SiW_{11}O_{39})(H_2O)_2] \cdot 24H_2O$ (1). A 2.28 g (0.71 mmol) sample of $K_8[SiW_{11}O_{39}] \cdot 13H_2O$ was dissolved in 5 mL of water at 80 °C, followed by a dropwise addition of 550 mg (1.42 mmol) of $YbCl_3 \cdot 6H_2O$ in 5 mL of water. After 1 h, the solution was cooled to room temperature, and 720 mg (4.26 mmol) of CsCl was added. The resulting precipitate was filtered, washed with EtOH, and dried with Et_2O . The resulting white powder was dissolved in water and allowed to crystallize at room temperature. After 1 week, white needles of **1**, suitable for X-ray diffraction, were collected, washed with EtOH, and dried with Et_2O . Yield: 2.23 g (81%). IR (KBr pellets, ν/cm^{-1}): 1006 (m), 947 (s), 888 (s), 824 (s), 798 (s), 690 (m), 539 (m). Anal. Calcd for $KCs_4YbSiW_{11}O_{65}H_{52}$: K, 1.01; Cs, 13.59; Yb, 4.45; W, 52.04. Found: K, 0.85; Cs, 13.03; Yb, 4.38; W, 52.07.

Synthesis of $K_{0.5}Nd_{0.5}[Nd_2(\alpha-SiW_{11}O_{39})(H_2O)_{11}] \cdot 17H_2O$ (2a). A 3.48 mL (36 mmol) sample of $HClO_4$ (10.37 M) was added to a suspension of 2.02 g (6 mmol) of Nd_2O_3 in 20 mL of water. The resulting solution was heated to 80 °C for 1 h, and the pH adjusted to 5 by addition of 1.85 mL of a 0.4 M NaOH solution. Then, 6.58

g (2 mmol) of $K_8[SiW_{11}O_{39}] \cdot 13H_2O$ dissolved in 5 mL of water was added. After 1 h, the solution was cooled to room temperature, and a precipitate containing potassium perchlorate as the main product was removed by filtration. After 1 night, a pale pink precipitate was filtered. The obtained powder was allowed to crystallize at room temperature after dissolution in water. After 3 days, pale pink needles of **1a**, suitable for X-ray diffraction, were collected, washed with EtOH, and dried with Et_2O (2.35 g, 35%). IR (KBr pellets, ν/cm^{-1}): 1004 (m), 947 (s), 886 (s), 827 (s), 799 (s), 701 (m), 542 (m). Anal. Calcd for $K_{0.5}Nd_{2.5}SiW_{11}O_{67}H_{56}$: K, 0.55; Nd, 10.13; W, 56.83. Found: K, 0.89; Nd, 9.70; W, 55.64.

Synthesis of $K_2[Nd_2(\alpha-SiW_{11}O_{39})(H_2O)_{11}] \cdot 11H_2O$ (2b). **2b** was prepared following the procedure described for **2a**, but using 1.16 mL (12 mmol) of $HClO_4$ (10.37 M) and 0.67 g (2 mmol) of Nd_2O_3 . Yield: 2.02 g (30%). IR (KBr pellets, ν/cm^{-1}): 998 (m), 955 (s), 905 (s), 855 (s), 802 (s), 689 (m), 543 (m). Anal. Calcd for $K_2Nd_2SiW_{11}O_{61}H_{44}$: K, 2.27; Nd, 8.39; W, 58.84. Found: K, 2.25; Nd, 8.46; W, 58.80.

Synthesis of $Na_{0.5}Cs_{4.5}[Eu(\alpha-SiW_{11}O_{39})(H_2O)_2] \cdot 23H_2O$ (3a). An 860 μL (9 mmol) sample of $HClO_4$ (10.37 M) was added to a suspension of 528 mg (1.5 mmol) of Eu_2O_3 in 15 mL of water. The resulting solution was heated to 80 °C for 1 h, and the pH adjusted to 5 by addition of 1.85 mL of a 0.4 M NaOH solution. Then, 1.610 g (0.5 mmol) of $K_8[SiW_{11}O_{39}] \cdot 13H_2O$ dissolved in 5 mL of water was added. After 1 h, the solution was cooled to room temperature and a precipitate containing potassium perchlorate as the main product removed by filtration. An 840 mg (5 mmol) sample of CsCl was then added, affording a white precipitate which was filtered. The obtained powder was allowed to crystallize at room temperature after dissolution in water. After 10 days, white needles of **1a**, suitable for X-ray diffraction, were collected, washed with EtOH, and dried with Et_2O . Yield: 0.96 g (50%). IR (KBr pellets, ν/cm^{-1}): 998 (m), 950 (s), 893 (s), 824 (s), 793 (s), 688 (m), 545 (m). Anal. Calcd for $Na_{0.5}Cs_{4.5}EuSiW_{11}O_{64}H_{50}$: Na, 0.29; Cs, 15.39; Eu, 3.91; W, 52.04. Found: Na, 0.24; Cs, 15.38; Eu, 3.95; W, 50.97. **3a** can also be obtained using 290 μL (3 mmol) of $HClO_4$ (10.37 M) and 176 mg (0.5 mmol) of Eu_2O_3 .

Synthesis of $KCs_4[Eu(\alpha-SiW_{11}O_{39})(H_2O)_2] \cdot 10H_2O$ (3b). **3b** was prepared following the procedure described for **1**, but using $EuCl_3 \cdot 6H_2O$ (520 mg, 1.42 mmol) as the rare-earth reagent. Yield: 2.38 g (93%). IR (KBr pellets, ν/cm^{-1}): 999 (m), 948 (s), 891 (s), 826 (s), 795 (s), 722 (m), 684 (m), 542 (m). Anal. Calcd for $KCs_4EuSiW_{11}O_{51}H_{24}$: K, 1.08; Cs, 14.71; Eu, 4.21; W, 55.97. Found: K, 0.95; Cs, 14.91; Eu, 4.36; W, 56.10.

Synthesis of $K_5[Eu(\alpha-SiW_{11}O_{39})(H_2O)_2] \cdot 18H_2O$ (3c). A 2.28 g (0.71 mmol) sample of $K_8[SiW_{11}O_{39}] \cdot 13H_2O$ was dissolved in 5 mL of water at 80 °C, followed by a dropwise addition of 520 mg (1.42 mmol) of $EuCl_3 \cdot 6H_2O$ in 5 mL of water. After 1 h, 320 mg (4.26 mmol) of KCl was added. The solution was cooled to room temperature, and after 1 night the resulting precipitate was filtered, washed with EtOH, and dried with Et_2O . Yield: 2.14 g (89%). IR (KBr pellets, ν/cm^{-1}): 1002 (m), 949 (s), 891 (s), 825 (s), 795 (s), 680 (s), 543 (m). Anal. Calcd for $K_5EuSiW_{11}O_{59}H_{40}$: K, 5.78; Eu, 4.49; W, 59.79. Found: K, 6.02; Eu, 4.21; W, 59.51.

Synthesis of $K_5[Eu(\alpha-SiW_{11}O_{39})(H_2O)_2] \cdot nD_2O$ (3d). **3d** was prepared following the procedure described for **3c**, but using D_2O as the solvent and working under a nitrogen atmosphere.

Synthesis of $KCs_4[Gd(\alpha-SiW_{11}O_{39})] \cdot 25H_2O$ (3e). **3e** was prepared following the procedure described for **3b**, but using $GdCl_3 \cdot 6H_2O$ (528 mg, 1.42 mmol) as the rare-earth reagent. Yield: 2.30 g (85%). IR (KBr pellets, ν/cm^{-1}): 1001 (m), 947 (s), 891 (s), 829 (s), 801 (s), 683 (m), 542 (m). Anal. Calcd for KCs_4

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Table 1. Crystallographic Data for **1**, **2a**, and **3a**

	1	2a	3a
empirical formula	H ₅₂ SiKCs ₄ O ₆₅ W ₁₁ Yb	H ₅₆ SiK _{0.5} O ₆₇ W ₁₁ Nd _{2.5}	H ₅₀ SiNa _{0.5} O ₆₄ W ₁₁ EuCs _{4.5}
fw	3886.7	3558.5	3287.8
cryst syst	orthorhombic	triclinic	monoclinic
space group	<i>Pnm</i> 2(1) (No. 31)	<i>P</i> 1̄ (No. 2)	<i>P</i> 2(1)/ <i>c</i> (No. 14)
<i>a</i> , Å	16.4189(2)	12.4824(1)	11.5262(4)
<i>b</i> , Å	12.9208(2)	12.7297(2)	22.3425(7)
<i>c</i> , Å	11.29910(10)	18.6815(1)	18.9907(6)
α , deg	90	86.877(1)	90
β , deg	90	80.152(1)	100.347(1)
γ , deg	90	82.993(1)	90
<i>V</i> , Å ³	2397.05(5)	2901.14(5)	4811.0(3)
<i>Z</i>	2	2	4
ρ_{calcd} , g cm ⁻³	4.847	3.872	5.063
μ , mm ⁻¹	31.406	24.068	31.331
<i>T</i> , K	296(2)	296(2)	296(2)
no. of data/params	6120/301	8030/646	12613/617
<i>R</i> (<i>I</i> > 2 σ (<i>I</i>))	R1(<i>F</i> _o) ^a = 0.0569 wR2(<i>F</i> _o ²) ^b = 0.1479	R1(<i>F</i> _o) ^a = 0.0603 wR2(<i>F</i> _o ²) ^b = 0.1404	R1(<i>F</i> _o) ^a = 0.0387 wR2(<i>F</i> _o ²) ^b = 0.0726
<i>R</i> (all data)	R1(<i>F</i> _o) ^a = 0.0612 wR2(<i>F</i> _o ²) ^b = 0.1504	R1(<i>F</i> _o) ^a = 0.0876 wR2(<i>F</i> _o ²) ^b = 0.1511	R1(<i>F</i> _o) ^a = 0.0634 wR2(<i>F</i> _o ²) ^b = 0.0807

$$^a R1 = \sum |F_o| - |F_c| / \sum |F_c|. \quad ^b wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**, **2a**, and **3a**

	1	2a	3a
W–O _a	2.291(13)–2.385(17)	2.204(15)–2.417(16)	2.225(7)–2.419(7)
W–O _{b,c}	1.739(16)–2.046(16)	1.724(15)–2.096(17)	1.756(7)–2.095(7)
W–O _d	1.666(17)–1.733(16)	1.62(3)–1.735(17)	1.709(7)–1.754(7)
Si–O	1.60(2), 1.656(16)	1.601(18)–1.677(19)	1.616(7)–1.643(7)
Ln–O _{b,c}	2.272(15), 2.39(2)	2.433(15)–2.474(18)	2.342(7)–2.372(7)
Ln–O _d	2.39(2)	2.478(15)–2.522(17)	2.460(7), 2.542(7)
Ln–O _w ^a	2.32(2)	2.46(2)–2.58(2)	2.450(7), 2.454(8)
O–W–O _{cis}	70.5(6)–102.5(8)	70.5(6)–103.5(9)	71.5(3)–104.0(4)
O–W–O _{trans}	155.0(9)–173.0(8)	154.0(7)–173.0(8)	155.0(3)–172.0(3)
O–Si–O	106.9(8)–113.0(8)	108.0(9)–111.5(9)	108.0(4)–111.5(4)
O–Ln–O _{cis}	70.0(7)–87.5(8)	64.0(13)–92.5(11)	70.0(3)–80.5(3)
O–Ln–O _{trans}	123.0(9)–149.0(7)	108.5(7)–144.0(11)	108.0(2)–147.0(2)

^a The subscript “w” refers to a water oxygen atom.

GdSiW₁₁O₆₄H₅₀: K, 1.01; Cs, 13.80; Gd, 4.08; W, 52.50. Found: K, 1.05; Cs, 13.96; Gd, 4.27; W, 52.32.

Synthesis of K_{0.5}Cs_{4.5}[Gd_{0.92}Eu_{0.08}(α -SiW₁₁O₃₉)(H₂O)₂] \cdot 15H₂O (3f**).** **3f** was prepared following the procedure described for **3b**, but using a mixture of GdCl₃ \cdot 6H₂O (500 mg, 1.35 mmol) and EuCl₃ \cdot 6H₂O (26 mg, 0.07 mmol) as the rare-earth reagent. Yield: 2.38 g (89%). IR (KBr pellets, ν /cm⁻¹): 1001 (m), 948 (s), 891 (s), 828 (s), 800 (s), 688 (m), 542 (m). Anal. Calcd for K_{0.5}Cs_{4.5}-Gd_{0.9}Eu_{0.1}SiW₁₁O₅₆H₃₄: K, 0.51; Cs, 15.73; Gd, 3.80; Eu, 0.32; W, 53.20. Found: K, 0.38; Cs, 16.08; Gd, 3.80; Eu, 0.44; W, 53.00.

X-ray Crystallography. Intensity data collection was carried out with a Siemens SMART three-circle diffractometer equipped with a CCD detector using Mo K α monochromatized radiation (λ = 0.71073 Å). The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using the SADABS program¹¹ based on the method of Blessing.¹² The structures were solved by direct methods and refined by full-matrix least-squares using the SHELX-TL package.¹³ Crystallographic data are given in Table 1. Selected bond distances are listed in Table 2.

Optical Spectroscopy. Luminescence spectra were recorded on powder samples at room temperature and 77 K as well as in solution

at room temperature with excitation coming from an OPO (optical parametric oscillator) pumped by the third harmonic of a Q-switched Nd:YAG laser, at wavelengths corresponding to the ⁷F₀ \rightarrow ⁵D₂ absorption transitions. An intensified optical multichannel analyzer (OMA) is used for the detection of the luminescence. With this apparatus, it is also possible to record the emission at various times after the laser pulse and therefore to obtain the lifetime decay profiles.

Elemental analysis was performed by the Service Central d'Analyse of CNRS, 69390 Vernaison, France.

Infrared spectra (KBr pellets) were recorded on an IRFT Nicolet 550 apparatus.

Results

Synthesis. The reactivity of the [α -SiW₁₁O₃₉]⁸⁻ monovan- cant polyoxometalate with lanthanide has been investigated for four different trivalent rare-earth cations (Ln = Nd^{III}, Eu^{III}, Gd^{III}, Yb^{III}). The europium compound has been prepared using both EuCl₃ and Eu(ClO₄)₃ as the lanthanide source and isolated as a cesium or a potassium salt. In all cases, the pH has been controlled and maintained between 4 and 5. The compounds are obtained in a moderate to good yield. Elemental analysis, IR spectroscopy, and TGA studies have shown that the crude and recrystallized products have the same composition. Single crystals of **1**, **2a**, **3a**, and **3e** have

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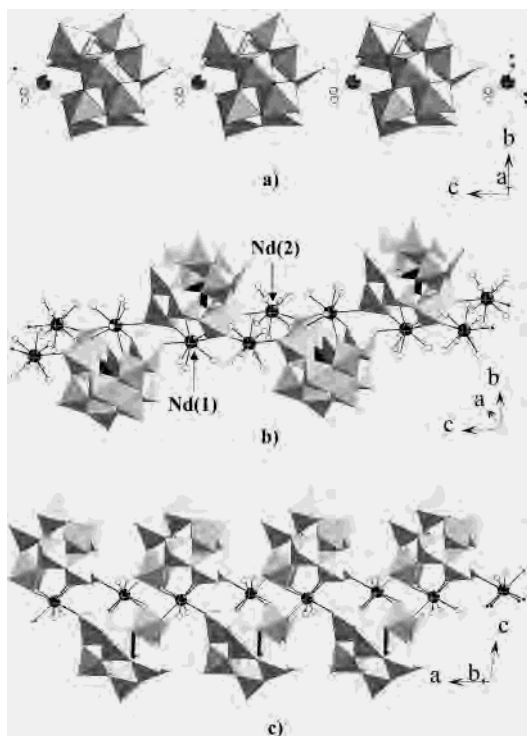


Figure 1. Polyhedral representation of $[Yb(\alpha-SiW_{11}O_{39})(H_2O)_2]^{5-}$ showing the infinite one-dimensional linear arrangement of the $[\alpha-SiW_{11}O_{39}]^{8-}$ polyanions (a) and polyhedral representation of $[Nd_2(\alpha-SiW_{11}O_{39})(H_2O)_{11}]^{2-}$ (b) and $[Eu(\alpha-SiW_{11}O_{39})(H_2O)_2]^{5-}$ (c) showing the infinite one-dimensional zigzag arrangement of the monovacant polyanions. Key: black cross-hatched circles, Ln; white circles, O; light gray octahedra, $\{WO_6\}$; black tetrahedra, $\{SiO_4\}$.

been obtained. Due to the low solubility of the cesium salts, potassium salts have been synthesized and used for optical studies of the europium compound in aqueous solution (see below).

Solid-State Structures of 1, 2a, and 3a. The solid-state structures of compounds **1** and **3a** consist of infinite one-dimensional arrangements built up of $[\alpha-SiW_{11}O_{39}]^{8-}$ anions connected by rare-earth cations, while the structure of **2a** consists of a bidimensional arrangement of this subunit. Crystal data are given in Table 1. $[\alpha-SiW_{11}O_{39}]^{8-}$ derives from the $[\alpha-SiW_{12}O_{40}]^{4-}$ anion formed of twelve $\{W^{VI}O_6\}$ octahedra forming four $\{W_3O_{13}\}$ fragments. These fragments are built up of $\{WO_6\}$ octahedra sharing edges via $W-O_c-W$ connections, and linked to the encapsulated silicon atom via a $W-O_a-Si$ bond. The $\{W_3O_{13}\}$ groups are connected to each other by vertices via O_b atoms. A terminal oxygen O_d completes the coordination sphere of the W centers. Finally, the monovacant species is obtained by the formal removal of a $W=O_d$ group. Bond lengths and angles relative to the tungsten octahedra constituting **1**, **2a**, and **3a** do not show unusual features (see Table 2).

The structure of **1** is represented in Figure 1a. The Yb^{3+} cation occupies the vacant site of an $[\alpha-SiW_{11}O_{39}]^{8-}$ subunit. The rare earth is coordinated to the four available oxygen atoms of the lacunary site ($d_{Yb-O_b} = 2.301(17)$ Å and $d_{Yb-O_c} = 2.272(15)$ Å). Connection of the $[\alpha-SiW_{11}O_{39}]^{8-}$ subunits occurs via $Yb-O_d$ bonds ($d_{Yb-O_d} = 2.39(2)$ Å). The coordination sphere of the ytterbium center is completed by

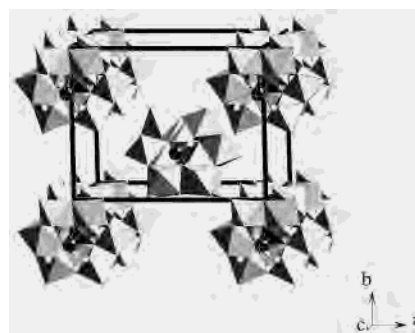


Figure 2. Polyhedral representation of $[Yb(\alpha-SiW_{11}O_{39})(H_2O)_2]^{5-}$ showing the two interpenetrated orthorhombic networks formed by the chains of the rare-earth polyanions running along the c axis. The unit cell edges are shown (black lines). Key: black cross-hatched circles, Yb; white circles, O; light gray octahedra, $\{WO_6\}$; black tetrahedra, $\{SiO_4\}$.

two water molecules ($d_{Yb-OH_2} = 2.32(2)$ Å) bridging the rare earth and a cesium counterion. The ytterbium center is thus heptacoordinated, and the local symmetry of the $[Yb(\alpha-SiW_{11}O_{39})(H_2O)_2]^{5-}$ building group is C_s . The monodimensional structure can then be described as a molecular wire of $[Yb(\alpha-SiW_{11}O_{39})(H_2O)_2]^{5-}$ with all the subunits running along the c axis. This arrangement is related to that found for $\{XMW_{11}O_{39}\}_n$ ($X = P, M = Mn^{II}; X = P$ or $As, M = Co^{II}$),^{3d,14} where the divalent transition metal present in the lacunary site is bound to five oxygen atoms of the host $[XW_{11}O_{39}]^{7-}$ polyanion and to a terminal $W=O_d$ oxygen atom of an adjacent $[XMW_{11}O_{39}]^{5-}$ subunit, leading to a linear monodimensional structure. The three-dimensional arrangement of **1** can be described considering that the polyanions are located at the vertices of two interpenetrated orthorhombic networks of edge lengths having the cell parameter values (Figure 2). It follows that the shortest intrachain and interchain Yb–Yb distances are comparable (11.30(2) and 11.53(2) Å, respectively).

The structure of **2** is represented in Figure 1b. As for compound **1**, a rare-earth cation occupies the vacant site of a $[\alpha-SiW_{11}O_{39}]^{8-}$ subunit and is coordinated to the four oxygen atoms of the lacunary site ($d_{Nd(1)-O} = 2.433(15)–2.474(18)$ Å). Nevertheless, the monodimensional arrangement of the neodymium compound is radically different from that found for **1**. The structure can be described as an assembly of dimers. Each dimer contains two $[\alpha-SiW_{11}O_{39}]^{8-}$ subunits connected by two Nd(1) centers via two O_d oxygen atoms ($d_{Nd-O_d} = 2.515(16)$ Å), an inversion center relating the $\{Nd(\alpha-SiW_{11}O_{39})(H_2O)_4\}$ parts. Connection of the dimeric $[Nd_2(\alpha-SiW_{11}O_{39})_2(H_2O)_8]^{10-}$ entities is ensured by four Nd(2) centers via O_d atoms ($d_{Nd-O_d} = 2.478(15)$ and 2.522(17) Å). The coordination spheres of the Nd(1) and the Nd(2) centers are completed by four and seven water molecules, respectively ($d_{Nd-OH_2} = 2.46(3)–2.58(2)$ Å). Thus, all the neodymium atoms are nonacoordinated. The resulting infinite chains $\{Nd_4(\alpha-SiW_{11}O_{39})_2(H_2O)_{22}\}_n$ are directed along the c axis, with relatively short intrachain Nd–Nd distances ($d_{Nd(1)-Nd(1)} = 6.75(2)$ Å). An additional important feature, compared to compound **1**, is that, instead of alkali-

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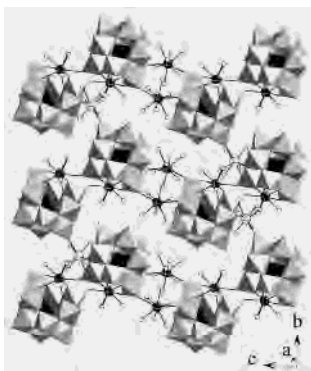


Figure 3. Bidimensional arrangement of $[\text{Nd}_2(\alpha\text{-SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_{11}]^{2-}$. The intrachain Nd^{3+} cations are represented by black cross-hatched circles. The Nd^{3+} cations connecting the chains are represented by white cross-hatched circles, taking into account the 25% occupation site found for these ions. Key: white circles, O; light gray octahedra, $\{\text{WO}_6\}$; black tetrahedra, $\{\text{SiO}_4\}$.

metal counterions, disordered lanthanide cations have been found connecting the chains. Resolution of the disorder revealed that **2a** possesses a bidimensional structure (Figure 3), only terminal neodymium being present between the *bc* planes containing the connected chains.

The structure of compound **3a** is closely related to that previously reported by Pope et al. for $(\text{NH}_4)_5[\text{Ce}(\alpha\text{-SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_3] \cdot 7\text{H}_2\text{O} \cdot (\text{NH}_4\text{Cl})_{0.5}$.¹⁰ The Eu^{3+} cation resides in the vacancy of the polyanion ($d_{\text{Eu}-\text{O}} = 2.347(1) - 2.368(1)$ Å) and is bound to two adjacent $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ subunits via two O_d oxygen atoms ($d_{\text{Eu}-\text{O}_d} = 2.458(1)$ and $2.543(1)$ Å). While three water molecules complete the coordination sphere of the cerium center, only two water ligands are bound to the Eu^{3+} center, which is then octacoordinated, adopting a distorted Archimedean antiprism geometry (pseudo- D_{4d}). As for **1** and **2a**, the exogenous ligands of the rare earth are connected to alkali-metal counterions. **3a** adopts a monodimensional arrangement with zigzag chains directed along the *a* axis (Figure 1c), with intrachain and shortest interchain Eu–Eu distances of 6.273(1) and 12.759(1) Å, respectively.

Discussion

General Information. The influence of several parameters has been studied to elucidate the main factors imposing the multidimensional arrangement of the $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ subunits. The europium compound can be obtained either from $\text{Eu}(\text{ClO}_4)_3$, prepared in situ, or from EuCl_3 , showing that the nature of the rare-earth counterion has no influence on the final product. Similarly, it is unlikely that the nature of the counteranion plays any significant role since $\text{KCs}_4[\text{Yb}(\alpha\text{-SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_2] \cdot 24\text{H}_2\text{O}$ and $\text{KCs}_4[\text{Gd}(\alpha\text{-SiW}_{11}\text{O}_{39})] \cdot 25\text{H}_2\text{O}$ ¹⁵ possess different topologies while $(\text{NH}_4)_5[\text{Ce}(\alpha\text{-SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_3] \cdot 7\text{H}_2\text{O} \cdot (\text{NH}_4\text{Cl})_{0.5}$ and $\text{Na}_{0.5}\text{Cs}_{4.5}[\text{Eu}(\alpha\text{-SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_2] \cdot 23\text{H}_2\text{O}$ exhibit analogous monodimensional arrangements. As compounds **1**, **2b**, and **3a** can be obtained in

similar conditions (i.e., the same $\text{Ln}/(\text{SiW}_{11}\text{O}_{39})^{8-}$ ratio (2:1), same temperature, same concentration of starting polyoxometalate, and same pH), it follows that the solid-state structures adopted by these compounds must be imposed by the nature of the rare earth used. The ionic radii of rare-earth cations diminish significantly from Ce^{3+} (1.14 Å) to Yb^{3+} (0.98 Å),¹⁶ and consequently, while the neodymium centers present in the chains are nonacoordinated in **2a**, the europium is octacoordinated in **3a** and the ytterbium heptacoordinated in **1**. Moreover, the coordination sphere of the ytterbium center in **1** can be deduced from that found for the lanthanide center in **3a** by the formal removal of an oxygen atom, O_d , linked to the europium cation. Then, it seems likely that the different monodimensional arrangements of the monovacant building blocks found for compounds **1** and **3a** are due to the difference in coordination of their respective lanthanide centers. An alternative proposition would be that, as the size of the lanthanide decreases, the repulsion between the vacant polyanions increases, provoking the transition from a zigzag to a linear organization of the $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ subunits. It is more difficult to justify the topology adopted by the neodymium compound **2a**. Nevertheless, it has to be noticed that this compound can be obtained in two forms, as a potassium salt (**2b**) or as a mixed potassium/neodymium salt (**2a**). Attempts to obtain analogous compounds of **1**, **3a**, and **3e** with the corresponding rare earth as the counterion have failed, even when a large excess of lanthanide was used, indicating that neodymium exhibits a unique affinity for the polyoxometalate studied.

Optical Spectroscopy. The luminescence of the europium ion in compounds **3a**, **3c**, **3d**, and **3f** has been studied under excitation into the $^5\text{D}_2$ level of the $4f^6$ configuration. For all these compounds the fluorescence spectra and the fluorescence decay time were recorded. In the same experimental conditions, the luminescence of europium in $\text{K}_{13}[\text{Eu}(\text{SiW}_{11}\text{O}_{39})_2] \cdot n\text{H}_2\text{O}$ has been reinvestigated, and our results are in good agreement with the data previously reported by Ballardini et al.⁹ Due to better resolution of our detection system, a small splitting of 12 cm^{-1} of the highest $^7\text{F}_1$ Stark component is observed. It indicates the presence of high local symmetry with at least a 3-fold axis for the europium local site. This splitting suggests an E symmetry assignment for this level, A being lower in energy. It is supported by the expected barycenter value for the $^7\text{F}_1$ manifold.¹⁷ Concerning the decay time of the $^5\text{D}_0$ state, the obtained value of 2.44 ms is in good agreement with that previously reported by Ballardini et al. (2.2 ms). The emission spectrum of $\text{K}_{13}[\text{Eu}(\text{SiW}_{11}\text{O}_{39})_2] \cdot n\text{H}_2\text{O}$ is shown in Figure 4 (top).

The high-resolution emission spectrum of the cesium salt **3a** in the solid state at 77 K is given in Figure 4 (bottom). The $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition, forbidden by the *J* selection rules, is observed due to the mixing with excited configurations with opposite parity through the low-symmetry crystal field components. As only one $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition is observed, the spectrum is consistent with a unique local site for the

(15) The cell parameters were determined by X-ray diffraction on a single crystal of **3d** (monoclinic, $a = 11.490(2)$ Å, $b = 22.338(3)$ Å, $c = 18.927(3)$ Å, $\beta = 100.57(2)^\circ$, $V = 4736$ Å³), showing that **3a** and **3d** are isostructural.

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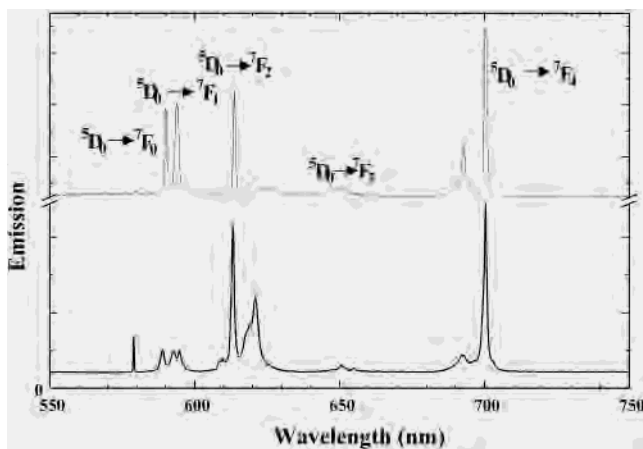


Figure 4. Emission spectra of $K_{13}[Eu(SiW_{11}O_{39})_2] \cdot nH_2O$ (top) and **3a** (bottom) in the solid state at 77K. The $^5D_0 \rightarrow ^7F_J$ ($J = 0-4$) emission lines were analyzed with a 75 cm focal length ARC monochromator equipped with a 1200 line/mm grating (blaze at 750 nm).

Eu^{3+} cations. $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions, respectively magnetic and electric dipole, are allowed by the J selection rules. They are clearly observed in the emission spectra. One can observe that the ratio of the $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ transitions is very different for $[Eu(SiW_{11}O_{39})_2]^{13-}$ and **3a**. Noncentrosymmetric low-symmetry sites lead to a predominant electric dipole transition and then to a large $^5D_0 \rightarrow ^7F_2/^5D_0 \rightarrow ^7F_1$ ratio. This is observed for **3a**. Moreover, the intensity of the $^5D_0 \rightarrow ^7F_0$ forbidden transition is larger in this compound. The degeneracy of the 7F_1 manifold is completely lifted. The emission spectrum indicates therefore that the local symmetry around the Eu^{3+} ions is lower in **3a**.¹⁸

It is known that the radiationless deactivation of the 5D_0 state is enhanced by the presence of terminal water molecules in the coordination sphere of the luminescent lanthanide center. Then, it was expected that the decay time would be found higher for $K_{13}[Eu(SiW_{11}O_{39})_2]$ (2440 μs),¹⁹ where the europium cation is coordinated to eight oxygen atoms of the two $[\alpha-SiW_{11}O_{39}]^{5-}$ subunits, than for compound **3a** (390 μs), where two water molecules are coordinated to the rare-earth center.

To determine whether energy transfer occurs between the europium ions along the chains of $\{Eu(SiW_{11}O_{39})(H_2O)_2\}_n$ in **3a**, the luminescence properties of the gadolinium compound doped with an 8% molar ratio of europium (**3f**) were studied. Such a comparison can be performed since the gadolinium and the europium compounds are isostructural. The spectra of **3a**, **3c**, and **3f** are quite similar. The decay lifetimes have been found to be comparable for **3a** and **3f** (respectively 390 and 380 μs). It follows that the luminescence properties of these compounds can be interpreted considering the lanthanide cations as isolated centers. Otherwise, the luminescence lifetime of the pure compound should be smaller than that of the diluted one. Another argument which confirms the absence of the energy migration

Table 3. Luminescence Decay Lifetimes τ of the 5D_0 State for Compounds **3a**, **3c**, **3d**, and **3f**

experimental conditions	sample	τ (μs)	experimental conditions	sample	τ (μs)
solid state, 300 K	3a $K_{13}[Eu(SiW_{11}O_{39})_2]$	390	solid state, 77 K	3c	340
	3c	2440		3d	860
	3f	370	solution, 300 K	3c	205
	3a	380		3d	1086
		390			

is that the 5D_0 lifetime of **3a** is not sensitive to temperatures between 300 and 77 K ($\tau = 390 \mu s$). The decay lifetimes have been measured for **3c** at room temperature and at 77 K (366 and 340 μs , respectively). The observed difference could be explained by the different degrees of hydration of these two compounds. Nevertheless, a water ligand has been found bridging the europium center to a cesium counterion in **3a**. It is then more likely to propose that the observed difference in lifetimes for these two compounds is due to a slight modification of the coordination sphere of the lanthanide when a potassium cation replaces a cesium cation. The decay times for the studied europium are gathered in Table 3.

Optical measurements also allow the determination of the number of coordinated water ligands n to a Eu^{III} center. The simple empirical law

$$n = 1.05(k_{H_2O} - k_{D_2O}) \pm 0.5$$

where k_{H_2O} and k_{D_2O} are the reciprocals of the experimental excited-state lifetime (ms) in H_2O and D_2O environment, respectively, has been established by Horrocks et al.²⁰ The deuterated analogue of **3c** (compound **3d**) has been prepared. Applying this relation to the lifetime values obtained for compounds **3c** and **3d** in the solid state at 77 K, it follows that, as in compound **3a**, two H_2O ligands complete the coordination sphere of the europium cation in **3c** ($n_{calcd} = 1.87 \pm 0.5$). More interestingly, the lifetime measurement of the 5D_0 state of **3c** in water solution and **3d** in deuterated water solution leads to a value of n of 4.15 ± 0.5 . This is a clear indication that the structure of **3c** collapses in water to give the $[Eu(SiW_{11}O_{39})(H_2O)_4]^{5-}$ complex, the europium center remaining octacoordinated. This is consistent with the fact that weak $Eu-O_d$ bonds are responsible for the multidimensional arrangement of the subunits in the solid state in compound **3a**.

Conclusion

We have then shown that the arrangement of the $[SiW_{11}O_{39}]^{8-}$ building units in the solid state can be tuned by choosing the appropriate lanthanide. The luminescent properties of the europium compound have been studied, proving that the monomeric species $[Eu(SiW_{11}O_{39})(H_2O)_4]^{5-}$ is obtained in water solution. It is interesting to note that the europium center is coordinated to four labile water molecules. We are currently working on the functionalization

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(19) The τ values given in the text refer to those measured at 300 K when no other indication is given.

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of lanthanide polyoxometalate complexes²¹ by multidentate ligands.²² The $[\text{Ln}(\text{SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_n]^{5-}$ complexes must be good candidates for the design of complex architectures, and indeed, the first attempts performed in our group are very promising.

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Supporting Information Available: Three X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC020486F

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