

Synthesis and electrochemical behavior of $[\text{SiW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{H}_2\text{O})]^{5-}$ and its oxo-bridged dimeric complex $[\text{SiW}_{11}\text{O}_{39}\text{Ru}^{\text{IV}}\text{ORu}^{\text{III}}\text{SiW}_{11}\text{O}_{39}]^{11-}$

Masahiro Sadakane^{*a,b} and Michio Higashijima^c

^a Organometallic Chemistry Laboratory, RIKEN (The Institute for Physical and Chemical Research), 2-1 Hirosawa, Wako, 351-0198, Japan

^b Catalysis Research Center, Hokkaido University, N-11, W-10, Sapporo, 060-0811, Japan. E-mail: sadakane@cat.hokudai.ac.jp

^c Homogeneous Catalysis Laboratory, MCC-Group Science and Technology Research Center, Mitsubishi Chemical Corporation, 1000 Kamoshida-cho, Aoba-ku, Yokohama, 227-8502, Japan. E-mail: 3001714@cc.m-kagaku.co.jp

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Caesium salts of mono-ruthenium(III) substituted Keggin-type silicopolytungstate ($[\text{SiW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{H}_2\text{O})]^{5-}$ (**1**)) and its oxo-bridged dimeric species ($[\{\text{SiW}_{11}\text{O}_{39}\text{Ru}^{\text{IV}}\}_2\text{O}]^{11-}$ (**8**)) were prepared and characterized by elemental analysis, infrared-spectroscopy, UV-Vis spectroscopy, and cyclic voltammetry for the first time. Both complexes could be isolated in pure form by hydrothermal reaction of $\text{K}_8[\text{SiW}_{11}\text{O}_{39}]$ and $\text{Ru}(\text{acac})_3$ followed by precipitation with CsCl . At low concentration (16 mM of Ru and $[\text{SiW}_{11}\text{O}_{39}]$, respectively), only the monomeric complex was obtained, whereas increasing the concentration of both reagents produced the dimeric species as a side product. Cyclic voltammetry showed that **1** was reversibly reduced to the aquaruthenium(II) derivative, oxidized to the oxoruthenium(IV), hydroxyruthenium(IV), and aquaruthenium(IV) complex depending on the pH of the solution, and further oxidized to the oxoruthenium(V) complex. The $\text{p}K_a$ value of the aquaruthenium(IV) and the hydroxyruthenium(IV) complex was estimated to be *ca.* 1.8 and 3.3, respectively. The dimeric complex (**8**) could be reversibly oxidized to the Ru(IV)–O–Ru(IV) derivative, reduced to the Ru(III)–O–Ru(III) complex and further to the Ru(III)–O–Ru(II) complex. The Ru(III)–O–Ru(II) complex disproportionates to the monomeric complex.

Introduction

Transition-metal substituted heteropolytungstates have attracted increasing interest because of their high activity as oxidation catalysts.¹ From the “parent” heteropolytungstate (“Keggin-type” $[\text{XW}_{12}\text{O}_{40}]^{n-}$; X = P ($n = 3$), Si ($n = 4$) or “Wells–Dawson-type” $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$), the so-called “lacunary” heteropolytungstate ($[\text{XW}_{11}\text{O}_{39}]^{n-}$; X = P ($n = 7$), Si ($n = 8$) or $[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$) can be derived by removing one WO unit. Many transition metals can fill this vacancy, giving rise to mono-transition-metal substituted heteropolytungstates such as $[\text{SiW}_{11}\text{O}_{39}\text{Co}^{\text{II}}(\text{H}_2\text{O})]^{6-}$. These complexes have been recognized as inorganic analogs of metalloporphyrin complexes and utilized as homogeneous oxidation catalysts. They have advantages over organometallic complexes; (1) they are robust under strongly oxidative conditions, under which most organic ligands decompose, (2) they can be used in both polar and non-polar solvents, (3) their redox properties are adjustable by changing the central (hetero) atom and the transition metal.

Recently, considerable attention has been directed towards ruthenium-substituted heteropolytungstates, because of the unique redox and catalytic properties of ruthenium metal. However, it is difficult to incorporate ruthenium metal into the lacunary site. Several articles have been devoted to the preparation of $[\text{SiW}_{11}\text{O}_{39}\text{Ru}]$,² $[\text{PW}_{11}\text{O}_{39}\text{Ru}]$,³ and $[\text{P}_2\text{W}_{17}\text{O}_{61}\text{Ru}]$ ⁴ complexes, but some of them were unsuccessful and the reported characterization data were questionable.

The ruthenium-substituted silicotungstate, $[\text{SiW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{H}_2\text{O})]^{5-}$, was first reported to be obtained by the reaction of $\text{K}_8[\text{SiW}_{11}\text{O}_{39}]$ with $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$,^{2a,b} and the thus-produced complex has been used as a catalyst for both oxidation and reduction reactions.^{2a,b,5} However, the thus-prepared material was an electrochemically inactive Ru-complex^{2d} and has alternatively been proposed to be a mixture of undefined complexes.^{1d,3a,4a} This complexity has been explained by the fact that

the commercially available $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ is a complicated mixture of mono- to poly-meric Ru compounds, with oxidation states of three and four.⁶

On the other hand, Rong and Pope succeeded in the synthesis of $\text{Cs}_4[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{H}_2\text{O})]$, by reacting $\text{K}_7[\text{PW}_{11}\text{O}_{39}]$ and $[\text{Ru}^{\text{II}}(\text{H}_2\text{O})_6][\text{C}_7\text{H}_7\text{SO}_3]_2$ followed by oxidation with molecular oxygen.^{3a} The isolated complex was well characterized using P- and W-NMR and cyclic voltammetry. The incorporated ruthenium is electrochemically active and produces the corresponding aquaruthenium(II), oxoruthenium(IV), and oxoruthenium(V) complexes in aqueous solution. The electrochemically-produced oxoruthenium(V) complex was reported to be an active species capable of oxidizing sulfoxide^{3a} and alcohol^{3d} compounds to the corresponding sulfone and carbonyl compounds, respectively.

This procedure, however, could not be used to prepare the silicon derivative, $[\text{SiW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{H}_2\text{O})]^{5-}$.^{3a} A novel method of preparing $[\text{SiW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{H}_2\text{O})]^{5-}$ in pure form is still needed.

The reaction of $[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ with $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ also produced a complex mixture, and the only ruthenium complex successfully identified was the μ -oxo-bridged-dimer, $\text{KLi}[\text{O}\{\text{Ru}^{\text{IV}}\text{Cl}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})\}_2]$.^{4a} In this dimeric complex, the ruthenium atoms are not incorporated in the “lacunary” site but are placed over the “lacunary” site. Recently, Nomiya *et al.* reported the synthesis of $[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}\text{Ru}^{\text{III}}(\text{H}_2\text{O})]^{7-}$ by reacting $\text{K}_{10}[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]$ and *cis*- $[\text{Ru}^{\text{II}}\text{Cl}_2(\text{dmsO})_4]$ followed by oxidation with Br_2 .^{4c}

In a preliminary paper, one of us reported the first synthetic procedure for preparing $[\text{SiW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}]^{5-}$ by reacting $\text{K}_8[\text{SiW}_{11}\text{O}_{39}]$ with $\text{Ru}(\text{acac})_3$ under hydrothermal conditions. The produced complex showed notable activity in the air oxidation of alkylaromatics at 200 °C in water media.^{2d} In this paper, we would like to describe the preparation, structural characterization, and electrochemical behavior of $[\text{SiW}_{11}\text{O}_{39}\text{Ru}]^{n-}$ and its oxo-bridged dimeric complex, $[\{\text{SiW}_{11}\text{O}_{39}\text{Ru}\}_2\text{O}]^{n-}$.

Experimental

Materials

All chemicals were reagent grade and used as supplied. Water was purified by passage through a purification train. $K_8[SiW_{11}O_{39}] \cdot 13H_2O$ was prepared according to a published method⁷ and was identified by infrared spectroscopy.

Synthesis of $Cs_5[SiW_{11}O_{39}Ru^{III}(H_2O)] \cdot 15H_2O$. $Ru(acac)_3$ (0.135 g, 0.34 mmol), $K_8[\alpha-SiW_{11}O_{39}] \cdot 13H_2O$ (0.996 g, 0.33 mmol), and 20 mL deaerated water were poured into a 100-mL autoclave and purged with Ar at 0.8 MPa. After the reaction was carried out at 220 °C (oil bath temperature) for 5 hours, the autoclave was cooled to room temperature for 2 hours. After the solution was filtered, CsCl (0.5 g) was added to the filtrate, and the solution was stirred at room temperature for 1 hour. The produced precipitates were filtered off, and CsCl (1.0 g) was added to the filtrate. After the solution was stirred at room temperature for 30 minutes, the solution was allowed to stand in a refrigerator overnight. The produced black solid (0.90 g) was filtered off, washed with ethanol and acetone to remove any unreacted $Ru(acac)_3$, and dried in air. The black solid was recrystallized twice from hot water to obtain the desired complex (0.54 g, 55 mol% based on W). Elemental analysis found: Cs, 17.50; W, 54.00; Si, 0.79; Ru, 2.66; H, 0.23; requires Cs, 17.82; W, 54.24; Si, 0.75; Ru, 2.71; H, 0.87%. Infrared spectrum (ν_{max}/cm^{-1}): 1007 (w), 989 (w), 962 (s), 915 (vs), 883 (s), 868 (s), 780 (vs).

Synthesis of $Cs_{11}[\{SiW_{11}O_{39}Ru^{IV(III)}\}_2O] \cdot 12H_2O$. $Ru(acac)_3$ (0.797 g, 2.00 mmol), $K_8[\alpha-SiW_{11}O_{39}] \cdot 13H_2O$ (5.962 g, 2.00 mmol), and 20 mL deaerated water were poured into a 100-mL autoclave and purged with Ar at 0.8 MPa. After the reaction was carried out at 220 °C (oil bath temperature) for 5 hours, the autoclave was cooled to the room temperature for 2 hours. After the solution was filtered, 100 mL of H_2O and then CsCl (3.0 g) were added to the filtrate, and the solution was stirred at room temperature for 1 hour. The produced precipitates were filtered off, and CsCl (6.0 g) was added to the filtrate. After the solution was stirred at room temperature for 30 minutes, the solution was allowed to stand in refrigerator overnight. The produced brown solid (4.58 g) was filtered off, washed with ethanol and acetone to remove any unreacted $Ru(acac)_3$, and dried in air. The brown solid was washed with hot water to obtain the desired complex (0.85 g, 12 mol% based on W). Elemental analysis found: Cs, 20.05; W, 55.82; Si, 0.80; Ru, 2.99; H, 0.23; requires Cs, 20.18; W, 55.83; Si, 0.78; Ru, 2.79; H, 0.33%. Infrared spectrum (ν_{max}/cm^{-1}): 1007 (w), 963 (s), 915 (vs), 883 (s), 788 (vs), 753 (s).

Physical measurements

Cyclic voltammetry was carried out at ambient temperature under argon on a CHI600A System (ALS). A glassy carbon working electrode (diameter, 3 mm), a platinum wire counter electrode and a Ag/AgCl reference electrode (3 M NaCl, Bioanalytical Systems, Inc.) were used. The initial potential was 0 V and the initial scan direction was towards more positive potential. Approximate formal potential values $E_{1/2}$ were calculated from the cyclic voltammograms as the average of the cathodic and anodic peak potentials for each corresponding oxidation and reduction wave. Controlled potential electrolysis was carried out using a BAS bulk electrolysis cell under argon atmosphere, and the progress was monitored by UV-Vis spectroscopy. FT-IR spectra were recorded by the KBr method with a Perkin-Elmer Paragon 1000 Fourier-transform infrared spectrometer with 2 cm^{-1} resolution. UV-Vis spectra were recorded at ambient temperature using a UV-2400PC spectrometer (Shimadzu) with a 1-cm quartz cell. Elemental analysis was carried out in the Characterization Center, Chemical

Analysis Division, at RIKEN. Ru, W, Si, and K were analyzed by the ICP method, Cs was analyzed by atomic absorption, and Cl was analyzed by ion chromatography. The water content of the isolated salts was calculated from thermogravimetric measurements, using a TG-8120 (RIGAKU), based on the total loss in weight up to 350 °C.

Results and discussion

Preparation and characterization of $[SiW_{11}O_{39}Ru^{III}(H_2O)]^{5-}$

The monomeric complex could be prepared from the hydrothermal reaction of the "lacunary" silicotungstate, $K_8[SiW_{11}O_{39}]$, and $Ru(acac)_3$ (ca. 16 mM, respectively) under inert atmosphere and isolated as its caesium salt by adding CsCl (for details, see the Experimental section). The FT-IR spectrum of the isolated complex showed the typical Keggin ($[SiW_{11}O_{39}M]^{n-}$) structure (Fig. 1 (a)), indicating the presence of the

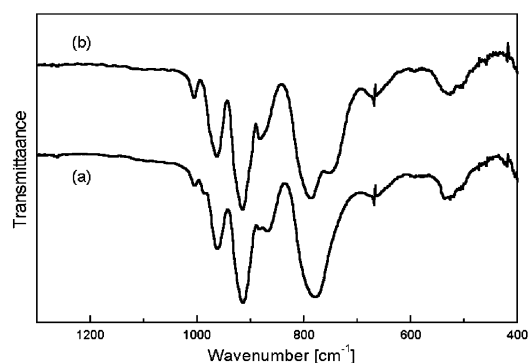


Fig. 1 IR spectra of (a) 1 and (b) 8.

Keggin unit. The elemental analysis of the isolated complex exhibited a Cs/Si/W/Ru ratio of 5 : 11 : 1, whereas neither Cl nor K was detected. These data demonstrated that the chemical formula of the isolated complex was $Cs_5SiW_{11}O_{39}Ru^{III}$.

Similar to the $[PW_{11}O_{39}Ru]$ complex,^{3a} a cyclic voltammogram of the isolated complex showed three well-defined redox pairs. Fig. 2 shows a cyclic voltammogram of a 1 mM

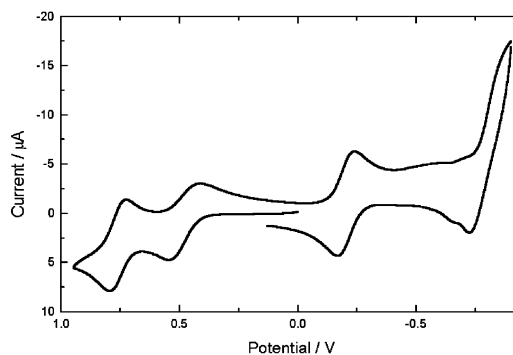


Fig. 2 Cyclic voltammogram of 1 (1 mM) in 0.5 M KH_2PO_4 solution (pH 4.5).

solution of the isolated complex in 0.5 M KH_2PO_4 solution (pH 4.5). Three well-defined reversible redox pairs ($E_{1/2} = 762$ mV, 487 mV, and -202 mV) and one ill-defined redox pair ($E_{1/2} = ca. -0.8$ V) were observed. The peak separations of the well-defined couples are typically 60–90 mV, and the peak currents were linearly dependent on the square root of the voltage scan rate, indicating that the electrode process is diffusion-controlled. Controlled potential electrolysis confirmed that all the well-defined reversible redox pairs correspond to a single electron transfer. Furthermore, the UV-Vis spectrum (Fig. 3(d)) of the one-electron reduced species was similar to the UV-Vis

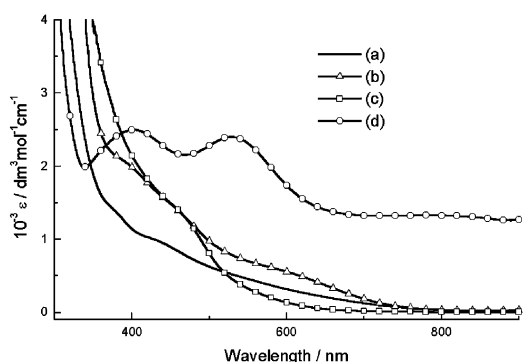


Fig. 3 UV-Vis spectra of $[\text{SiW}_{11}\text{O}_{39}\text{Ru}]$ in 0.5 M KH_2PO_4 (pH 4.5): (a) isolated complex, (b) one-electron oxidized complex, (c) two-electron oxidized complex, and (d) one-electron reduced complex.

spectrum of the $[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{II}}(\text{H}_2\text{O})]^{5-}$ complex.^{3a} Therefore, the well-defined reversible redox couples could be assigned to the Ru(v/iv), Ru(iv/iii), and Ru(iii/ii) redox systems, respectively, and the ill-defined reduction could be attributed to a two-electron reduction step of the $\text{SiW}_{11}\text{O}_{39}$ ligand by comparing the peak currents. Further reduction caused decomposition of the complex.⁸

The effect of the pH upon the redox potentials is summarized in Fig. 4. The Ru(iii/ii) redox potential was pH-independent

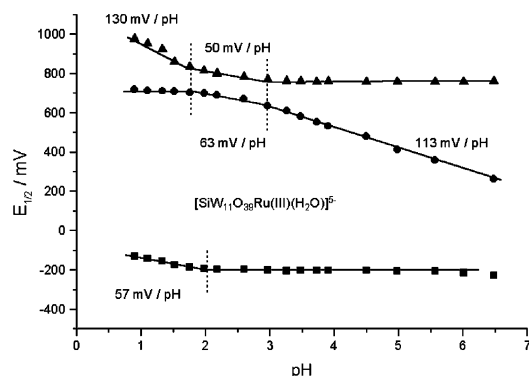
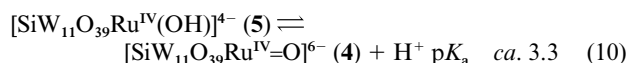
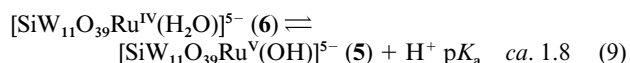
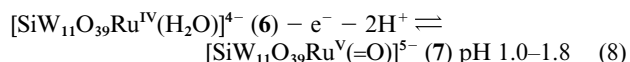
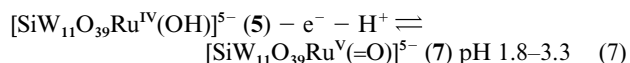
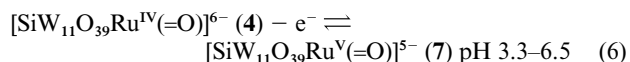
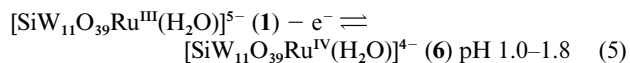
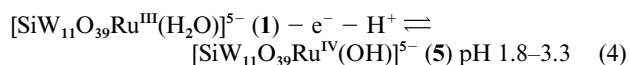
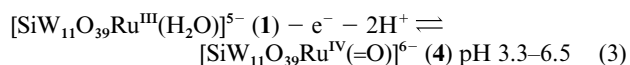
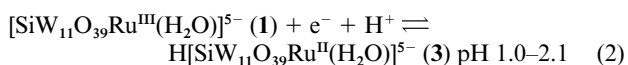
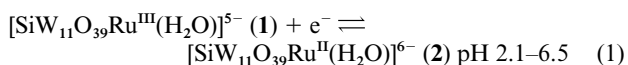
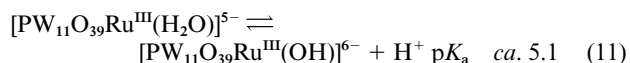


Fig. 4 pH dependence of $E_{1/2}$ for Ru(iii/ii) (■), Ru(iv/iii) (●), and Ru(v/iv) (▲).

from pH 2.1 to 6.5 but pH dependent from pH 1.0 to 2.1 with a slope of *ca.* 57 mV per pH unit, indicating that one proton was involved in the redox reaction below pH 2.1 (eqn. 1 and 2). Similar behavior has been reported in the case of the $[\text{SiW}_{11}\text{O}_{39}\text{Fe}^{\text{III}}(\text{H}_2\text{O})]^{5-}$ complex.⁹ The Ru(iv/iii) redox potential showed a linear dependence on the pH with a slope of *ca.* 113 mV and *ca.* 63 mV per pH unit in the pH ranges 3.3–6.5 and 1.8–3.3, respectively, but was independent of pH between pH 1 and 1.8. This means that two (eqn. 3), one (eqn. 4), and no protons (eqn. 5) are involved for this redox reaction. The tetravalent ruthenium complex exists as the aquaruthenium ($\text{Ru}^{\text{IV}}(\text{H}_2\text{O})$, (6)), hydroxyruthenium ($\text{Ru}^{\text{IV}}(\text{OH})$, (5)), or oxoruthenium ($\text{Ru}^{\text{IV}}(=\text{O})$, (4)) complex, depending on the pH of the solution. The redox potential of Ru(v/iv) was pH-independent between pH 3.3 and 6.5 but varied by *ca.* 50 mV per pH unit between pH 1.8 and 3.3 and *ca.* 130 mV per pH unit between pH 1.0 and 1.8, indicating that the pentavalent ruthenium exists only in the oxoruthenium ($\text{Ru}^{\text{V}}(=\text{O})$, (7)) complex in this pH range (eqn. 6–8). From this behavior, the pK_a of $\text{Ru}^{\text{IV}}(\text{H}_2\text{O})$ and $\text{Ru}^{\text{IV}}(\text{OH})$ could be estimated to be *ca.* 1.8 and *ca.* 3.3 (eqn. 9 and 10), respectively.



In the case of the $[\text{PW}_{11}\text{O}_{39}\text{Ru}]$ complex reported by Rong and Pope,^{3a} the pK_a (5.1) of the trivalent aquaruthenium complex, $[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{H}_2\text{O})]^{5-}$, has been observed (eqn. 11), and no protonation of the tetravalent oxoruthenium complex, $[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{IV}}(=\text{O})]^{5-}$, has been detected in the pH range 0–7. The difference between the $[\text{PW}_{11}\text{O}_{39}\text{Ru}]$ and $[\text{SiW}_{11}\text{O}_{39}\text{Ru}]$ complexes can be attributed to the higher negative charge of the $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ ligand compared to the $[\text{PW}_{11}\text{O}_{39}]^{7-}$ ligand. The $[\text{SiW}_{11}\text{O}_{39}\text{Ru}^{\text{IV}}(=\text{O})]^{6-}$ (4) complex could be protonated in acidic solution to produce the hydroxy (5) and aqua (6) complexes and its negative charge reduced, whereas less negative $[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{IV}}(=\text{O})]^{5-}$ was not protonated under the same conditions.



All experimental data, IR, elemental analysis, UV-Vis, and CV showed that the isolated complex was monomeric $\text{Cs}_5[\text{SiW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{H}_2\text{O})]$. The same reaction procedure was used to prepare other ruthenium-containing heteropolytungstates. The germanium derivative, $[\text{GeW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{H}_2\text{O})]^{5-}$, could be isolated in pure form.¹⁰ However, the reaction of $\text{Ru}(\text{acac})_3$ with $[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{39}]^{10-}$ produced $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ as a main product,¹¹ and the same reaction with $[\text{PW}_{11}\text{O}_{39}]^{7-}$ produced the desired complex ($[\text{PW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{H}_2\text{O})]^{4-}$) with unknown by-products, which could not be removed by recrystallization.

The electrochemical behavior of the germanium derivative, $[\text{GeW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{H}_2\text{O})]^{5-}$, was also examined. Similar to the silicon derivatives, the $[\text{GeW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{H}_2\text{O})]^{5-}$ complex could be reversibly oxidized to the $[\text{GeW}_{11}\text{O}_{39}\text{Ru}^{\text{IV}}(=\text{O})]^{6-}$ ($E_{1/2} = 478$ mV) and further to the $[\text{GeW}_{11}\text{O}_{39}\text{Ru}^{\text{V}}(=\text{O})]^{5-}$ ($E_{1/2} = 780$ mV) complex, and reduced to the $[\text{GeW}_{11}\text{O}_{39}\text{Ru}^{\text{II}}(\text{H}_2\text{O})]^{6-}$ ($E_{1/2} = -157$ mV) complex in aqueous solution (pH 4.5). Similar protonation of $[\text{GeW}_{11}\text{O}_{39}\text{Ru}^{\text{IV}}(=\text{O})]^{6-}$ could also be observed.

Isolation and characterization of $[\{\text{SiW}_{11}\text{O}_{39}\text{Ru}^{\text{IV/III}}\}_2\text{O}]^{11-}$

By increasing the concentration of the two reagents, $\text{Ru}(\text{acac})_3$ and $\text{K}_8[\text{SiW}_{11}\text{O}_{39}]$ (from 16 mM to 100 mM), a new species appeared as a side-product. Washing the crude sample with water could isolate this new complex (for details, see the Experimental section).

Although the IR spectrum of the new complex was similar to the IR spectrum of the monomeric complex (1) (compare

Figs. 1 (a) and (b), the UV-Vis spectra of both complexes were quite different. Although the UV-Vis spectrum of **1** showed no clear peak between 400 and 900 nm (Fig. 3 (a)), the UV-Vis spectrum of the new complex showed three intense peaks at 545 nm ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 14600), 437 nm ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 20600), and 372 nm ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 16200) (Fig. 5 (a)),

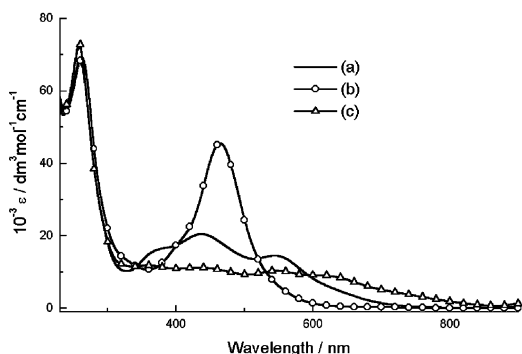


Fig. 5 UV-Vis spectra of $[\{\text{SiW}_{11}\text{O}_{39}\text{Ru}\}_2\text{O}]$ in 0.5 M KH_2PO_4 (pH 4.5): (a) isolated complex, (b) one-electron oxidized complex, (c) one-electron reduced complex.

indicating that the new complex contained the Keggin unit and that the environment of the ruthenium atom was different from that of **1**.

A cyclic voltammogram of the new complex in 0.5 M KH_2PO_4 (pH 4.5) solution showed two well-defined redox couples ($E_{1/2} = 588 \text{ mV}$ and -2 mV) and one ill-defined redox pair ($E_{1/2} = -280 \text{ mV}$), as shown in Fig. 6 (solid line). The peak

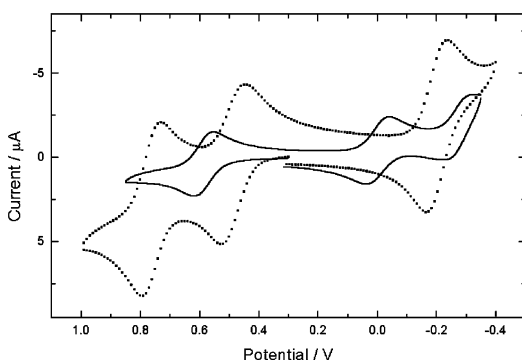


Fig. 6 Cyclic voltammograms of (···) the monomeric complex **1** (ca. 19 mg, 1 mM) and (—) the dimeric complex **8** (ca. 19 mg, 0.5 mM) in 5 mL of 0.5 M KH_2PO_4 solution (pH 4.5).

separation of the redox couple ($E_{1/2} = 588 \text{ mV}$) was ca. 59 mV and did not change on varying the voltage scan rate (25–169 mV s^{-1}). The peak currents were linearly dependent on the square root of the voltage scan rate, indicating that the electrode process was a reversible one-electron transfer.¹² The peak current of the new complex was about half of the peak current of the monomeric complex (**1**) when the same amount (ca. 19 mg) was dissolved in 5 mL of 0.5 M KH_2PO_4 (Fig. 6), demonstrating that the new complex contains one electrochemically active ruthenium site per two $[\text{SiW}_{11}\text{O}_{39}\text{Ru}]$ units. We proposed that the isolated complex was a dimeric complex ($[\{\text{SiW}_{11}\text{O}_{39}\text{Ru}\}_2\text{O}]^{11-}$), where two $[\text{SiW}_{11}\text{O}_{39}\text{Ru}]$ units were combined through a bridging oxygen (see Fig. 7), which is a common dimeric structure of the mono-transition-metal-substituted Keggin-type heteropolytungstate.^{13a,b}

Elemental analysis of the new complex demonstrated the presence of Cs/Si/W/Ru metals in a ratio of 11 : 2 : 22 : 2, and Cl and K were not detected. Furthermore, no weakly acidic proton was detected by acid–base titration, indicating that there was no protonated oxygen and that the negative charge of the new complex should be 11. Therefore, the isolated

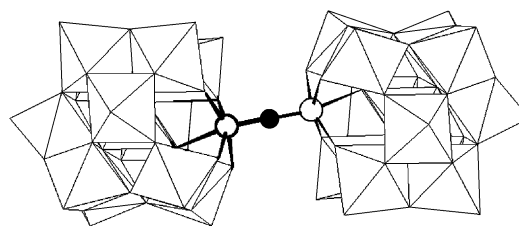


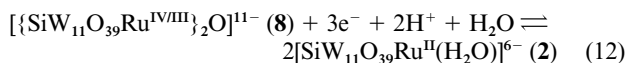
Fig. 7 Polyhedral representation of oxo-bridged dimeric complex $[\{\text{SiW}_{11}\text{O}_{39}\text{Ru}\}_2\text{O}]$ (○, ruthenium; ●, bridging oxygen).

product could be proposed to be a mixed-valent $\text{Cs}_{11}[\{\text{SiW}_{11}\text{O}_{39}\text{Ru}^{\text{IV/III}}\}_2\text{O}]$ complex.

Controlled potential electrolysis at 0.75 V confirmed that the mixed-valent $\text{Ru}(\text{IV})\text{–O–Ru}(\text{III})$ complex (**8**) could be oxidized to the $\text{Ru}(\text{IV})\text{–O–Ru}(\text{IV})$ complex. The UV-Vis spectrum of the $\text{Ru}(\text{IV})\text{–O–Ru}(\text{IV})$ complex showed a peak at 463 nm ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 45600) (Fig. 5 (b)). Re-reduction of the oxidized complex at 0.40 V re-confirmed that the redox process ($E_{1/2} = 588 \text{ mV}$) is a chemically reversible one-electron reaction.

The peak separation of the redox couple ($E_{1/2} = -2 \text{ mV}$) was about 80 mV, indicating that this process is an electrochemically quasi-reversible process. Controlled potential electrolysis at -0.13 V gave a charge of 1 F mol^{-1} for the net electrochemical reduction of the dimeric complex, and re-oxidation of the reduced solution quantitatively (net charge of 1 F mol^{-1}) produced the isolated species, which was monitored by UV-Vis spectroscopy. Therefore, this redox reaction could be attributed to the $\text{Ru}(\text{IV})\text{–O–Ru}(\text{III})/\text{Ru}(\text{III})\text{–O–Ru}(\text{III})$ process.

The ill-defined reduction peak ($E_{1/2} = -280 \text{ mV}$) could be estimated to be a one-electron process by comparing the peak currents. This process was chemically reversible on the time scale of the CV, but the reduced species was slowly converted to the monomeric complex. Controlled potential reduction of the one-electron reduced complex, $[\{\text{SiW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}\}_2\text{O}]^{12-}$, was done at -0.4 V . Two electrons per dimeric complex were consumed, and the monomeric divalent ruthenium complex, $[\text{SiW}_{11}\text{O}_{39}\text{Ru}^{\text{II}}(\text{H}_2\text{O})]^{6-}$ (**2**), was detected by CV and UV-Vis spectroscopy. This behavior, three electrons per dimeric complex were consumed to produce the two divalent monomeric complexes (**2**) from the isolated complex, also demonstrated that the new complex was a mixed-valent $[\{\text{SiW}_{11}\text{O}_{39}\text{Ru}^{\text{IV/III}}\}_2\text{O}]^{11-}$ complex (**8**) (eqn. 12). Similar reductive dissociation has been reported by Meyer *et al.* in the case of an oxygen-bridged polypyridine ruthenium complex.¹⁴



The dependence of each redox potential on the pH value is summarized in Figs. 8 and 9. The cyclic voltammogram of the complex in acidic (pH 1.5) solution showed one oxidative peak and two reduction peaks with the approximate current ratios of 1 : 1 : 2 (Fig. 8, ○), which could be assigned to the $\text{Ru}(\text{IV})\text{–O–Ru}(\text{IV})/\text{Ru}(\text{IV})\text{–O–Ru}(\text{III})$, $\text{Ru}(\text{IV})\text{–O–Ru}(\text{III})/\text{Ru}(\text{III})\text{–O–Ru}(\text{III})$, and $\text{Ru}(\text{III})\text{–O–Ru}(\text{III})/\text{Ru}(\text{II})\text{–O–Ru}(\text{II})$ redox reactions, respectively.

The two-electron redox pair ($\text{Ru}(\text{III})\text{–O–Ru}(\text{III})/\text{Ru}(\text{II})\text{–O–Ru}(\text{II})$) shifted in a more negative direction and separated into two one-electron peaks on increasing the pH of the solution. However, the redox waves were ill defined, and the peak separation was so large that a reasonable formal potential could not be obtained. Therefore, the pH effect on this redox reaction could not be examined.

By increasing the pH of the solution, the redox couple ($\text{Ru}(\text{IV})\text{–O–Ru}(\text{III})/\text{Ru}(\text{III})\text{–O–Ru}(\text{III})$) shifted to a more negative potential by about 130 mV per pH unit up to a pH of ca. 2.2 and by about 58 mV per pH unit between pH ca. 2.2 and ca. 4.6 and stopped shifting at a pH of ca. 4.6. This phenomenon

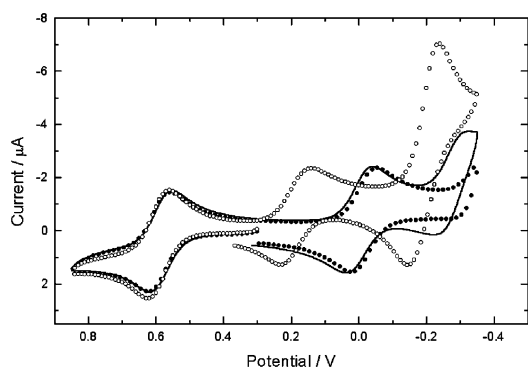


Fig. 8 Cyclic voltammograms of **8** in 0.5 M KHSO₄ (pH 1.5) solution (○), in 0.5 M KH₂PO₄ (pH 4.5) solution (—), and in 0.5 M K₂HPO₄ (pH 6.0) solution (●).

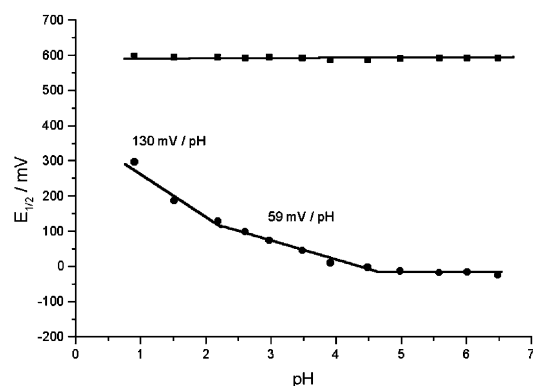
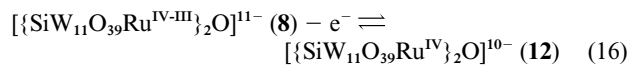
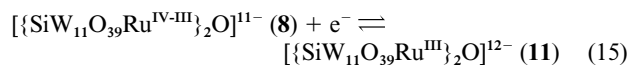
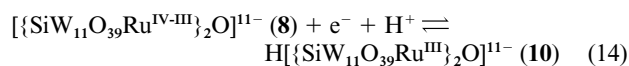
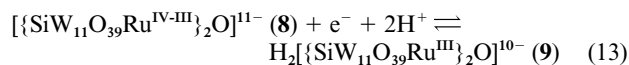


Fig. 9 pH dependence of $E_{1/2}$ for the Ru^{IV}ORu^{IV}/Ru^{IV}ORu^{III} (■) and Ru^{IV}ORu^{III}/Ru^{III}ORu^{III} (●) redox couples of the dimeric complex, [(SiW₁₁O₃₉Ru₂O)ⁿ⁻.

demonstrated that the reduced product, [(SiW₁₁O₃₉Ru^{III})₂O]¹²⁻ (**11**), was two (eqn. 13), one (eqn. 14), and no (eqn. 15) protons protonated in the pH range of < 2.2, 2.2–4.6, and > 4.6, respectively. The redox potential of Ru(IV)–O–Ru(IV)/Ru(IV)–O–Ru(III) was independent of the pH over the examined pH range, indicating that this redox process did not include any protons (eqn. 16).



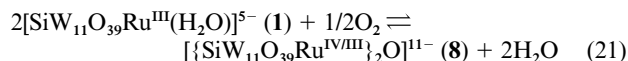
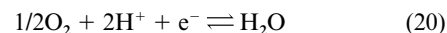
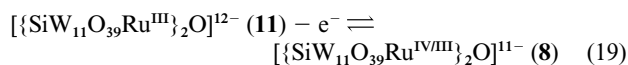
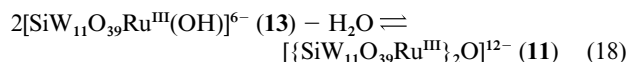
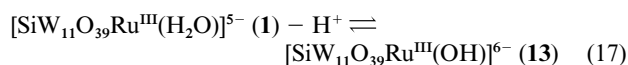
Formation of the dimeric complex, [(SiW₁₁O₃₉Ru^{IV/III})₂O]¹¹⁻

We propose that the mixed-valence complex (**8**) should be produced by dimerization (eqn. 17 and 18) of the deprotonated monomeric complex (**13**) followed by oxidation (eqn. 19) for the following reasons. (1) Oxidation of **11** to **8** occurred when the reaction solution was exposed to the air. The UV-Vis spectrum indicated that, just after the hydrothermal reaction under Ar atmosphere, the reaction mixture contained the dimeric trivalent complex (**11**), which was smoothly oxidized to the dimeric mixed-valent complex (**8**) if the solution was exposed to air (eqn. 19 and 20). (2) The higher concentration favored dimerization. Under the argon atmosphere, the dimeric complex was undetectable under low concentration (16 mM

of each starting compound) conditions. However, under high concentration (100 mM of each starting compounds) conditions a small amount of the dimeric complex could be detected. (3) This dimerization was promoted by the presence of base. The reaction of the monomeric complex (**1**, 16 mM) with an excess amount of Na(acac) under an argon atmosphere at 220 °C produced the dimeric complex, whereas **1** was intact without the Na(acac) under the same condition.

Similar dimerization of iron(III)-substituted silicotungstate, [SiW₁₁O₃₉Fe^{III}(OH)]⁶⁻,^{13a} and titanium(IV)-substituted phosphotungstate, [PW₁₁O₃₉Ti^{IV}(OH)]⁴⁻,^{13b} has been observed at ambient temperature. However, the dimerization of the ruthenium complex (**8**) needed a higher temperature. This dimerization proceeded not at room temperature but at a high temperature (220 °C).

The proposed dimerization reactions (eqn. 17–20) could be summarized by the oxidative dimerization reaction shown in eqn. 21. Indeed, the dimerization was also promoted by oxygen. When oxygen was introduced to the reaction (at 0.8 MPa, at 220 °C for 5 hours), the dimeric complex (**8**) could be produced even under low concentration conditions.



Conclusions

Mono-ruthenium(III)-substituted Keggin-type silicopolytungstate, [SiW₁₁O₃₉Ru^{III}(H₂O)]⁵⁻ (**1**), and its oxo-bridged dimeric species, [(SiW₁₁O₃₉Ru^{IV/III})₂O]¹¹⁻ (**8**), were isolated and characterized for the first time. Dimerization of the monomeric complex (**1**) to **8** changed its electrochemical properties. The monomeric complex (**1**) could be reversibly reduced to the aquaruthenium(II) complex, oxidized to the aquaruthenium(IV), hydroxyruthenium(IV), and oxoruthenium(IV) complexes depending on the pH, and further to the oxoruthenium(V) complex. On the other hand, the dimeric complex (**8**) could be reversibly oxidized/reduced to the Ru^{IV}-ORu^{IV}/Ru^{III}ORu^{III} complex, respectively. Further reduction to Ru^{III}ORu^{II} is reversible on the CV time scale, but the Ru^{III}ORu^{II} complex was disproportionated to the monomeric complex. In a preliminary paper,^{2d} one of us reported that the monomeric complex (**1**) showed high activity in the oxidation of *p*-xylene to terephthalic acid in water solvent. Investigation of the catalytic activity of the dimeric complex is our next project.

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