A γ-Keggin-type Dimeric Silicotungstate Sandwiching an Adamantanoid Tetra-nuclear Ruthenium–Oxygen Cluster Core

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A novel ruthenium-containing silicotungstate of $[(CH_3)_2NH_2]_8K_2H_2[(\gamma\text{-}SiW_{10}O_{36})_2Ru_4Cl_4O_2(OH)_4]\cdot 23H_2O$ (**1**) was obtained as a single crystal suitable for X-ray crystallographic analysis by the reaction of a divacant lacunary γ-Keggin silicotungstate $K_8[\gamma\text{-}SiW_{10}O_{36}]$ with $K_2[RuCl_5(OH_2)]$. The unprecedented dimeric silicotungstate consisted of two $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ units sandwiching an adamantanoid ruthenium–oxygen cluster core $[Ru_4Cl_4O_2(OH)_4]^{4+}$.

Polyoxometalates (POMs) are attractive compounds and used in the fields of analytical chemistry, medicine, electrochemistry, photochemistry, and catalysis.[1] Since the synthesis of the di-lacunary $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ (SiW_{10}) has been reported by Tézé and Hervé,[2] various kinds of monomeric di-metal-substituted POMs have also been reported.[3] Recently, the di-lacunary SiW_{10} unit has been utilized as a macroligand to encapsulate multinuclear metal–oxygen cluster cores, and the several dimeric and trimeric POMs based on the γ-Keggin units such as $[(\gamma\text{-}SiW_{10}O_{35})_2M(OH_2)_2]^{10-}$ ($M = Mn^{II}$, Co^{II}, and Ni^{II}), $[(\gamma\text{-}SiW_{10}O_{36})_2(PhSnOH_2)_2]^{10-}$, $[(\gamma\text{-}SiW_{10}O_{36})_2\{Ti_2(\mu\text{-}OH)_2(\mu\text{-}O)\}_2]^{8-}$, $[(\gamma\text{-}SiW_{10}O_{36})_2\{Cu_2(\mu\text{-}1,1\text{-}N_3)_2(H_2O)\}_2]^{12-}$, $[(\gamma\text{-}SiW_{10}O_{36})_2Cu_4(\mu\text{-}1,1,1\text{-}N_3)_2(\mu\text{-}1,1\text{-}N_3)_2]^{12-}$, $[\{(\gamma\text{-}SiW_{10}O_{36})Mn_2(\mu\text{-}OH)_2(H_2O)\}(\mu\text{-}1,3\text{-}N_3)\{(\gamma\text{-}SiW_{10}O_{36})Mn_2(\mu\text{-}OH)_2(N_3)\}]^{10-}$, $[(\gamma\text{-}SiW_{10}O_{36})_3\{Fe_2(\mu\text{-}OH)_3(H_2O)_2\}_3]^{15-}$, and $[(\gamma\text{-}SiW_{10}O_{36})_2Zr_2(\mu\text{-}OH)_2]^{10-}$ have been reported.[4]

Ruthenium is an attractive element because it displays a wide range of oxidation states and has the unique redox and catalytic properties.[5] Various kinds of ruthenium-containing POMs have been synthesized.[6] However, structurally characterized non-organometallic ruthenium-containing POMs are one of the least reported compounds, and syntheses of some compounds are difficult because of the mixed-valence nature of the precursors and of the difficulty of their purification.[7] Therefore, the novel structurally well-characterized ruthenium-containing POMs will provide significant values to this research area.

Here, we report the synthesis and structural characterization of a novel ruthenium-containing silicotungstate of $[(CH_3)_2NH_2]_8K_2H_2[(\gamma\text{-}SiW_{10}O_{36})_2Ru_4Cl_4O_2(OH)_4]\cdot 23H_2O$ (**1**). Complex **1** consisted of two SiW_{10} units sandwiching an adamantanoid tetranuclear ruthenium–oxygen cluster core, of which the presence was suggested in solution state.[8]

The ruthenium-containing POM **1** was synthesized by the reaction of a divacant lacunary γ-Keggin silicotungstate $K_8[\gamma\text{-}SiW_{10}O_{36}]$ with two equivalents of $K_2[RuCl_5(H_2O)]$ with respect to $K_8[\gamma\text{-}SiW_{10}O_{36}]$ in an aqueous solution at room temperature (ca. 295 K) as follows: To an aqueous solution (15 mL) of $K_8[\gamma\text{-}SiW_{10}O_{36}]\cdot 12H_2O$ (1.0 g, 0.36 mmol), $K_2[RuCl_5(H_2O)]$ (0.27 g, 0.72 mmol) was added in a single step. The pH of the solution was 5.0. After the solution was stirred for 5 min at room temperature, dimethylammonium chloride (1.0 g, 12 mmol) was added in a single step followed by filtration. Then, the filtrate was stand at room temperature. After three weeks, reddish brown needle-like crystals suitable for X-ray crystallographic analysis were collected by filtration and air-dried. The yield was relatively low (8%, see Supporting Information), presumably because of the high solubility of the product in aqueous media. The molecular structure of the anion part of **1** is shown in Figure 1. Selected bond lengths and angles are summarized in Table 1.[9]

The bond valence sum (BVS) values of ruthenium (3.95–4.55), tungsten (5.24–6.44), and silicon (4.11–4.16) indicate that the respective valences in **1** are +4, +6, and +4. The BVS values of O11, O21, O302, and O304 in the central adamantanoid cluster were 1.04, 1.03, 1.23, and 1.31, respectively and smaller than those of O301 (1.91) and O303 (2.34), suggesting that O11, O21, O302, and O304 are monoprotonated (μ-OH ligands) and that the central adamantanoid core in **1** is $[Ru_4Cl_4(\mu\text{-}O)_2(\mu\text{-}OH)_4]^{4+}$. The data of BVS, X-ray crystallographic analysis, elemental analysis, and thermogravimetric analysis show that the formula of **1** is $[(CH_3)_2NH_2]_8K_2H_2[(\gamma\text{-}SiW_{10}O_{36})_2Ru_4Cl_4O_2(OH)_4]\cdot 23H_2O$.

As shown in Figure 1, the polyanion **1** consisted of two lacunary SiW_{10} units sandwiching the adamantanoid tetra-

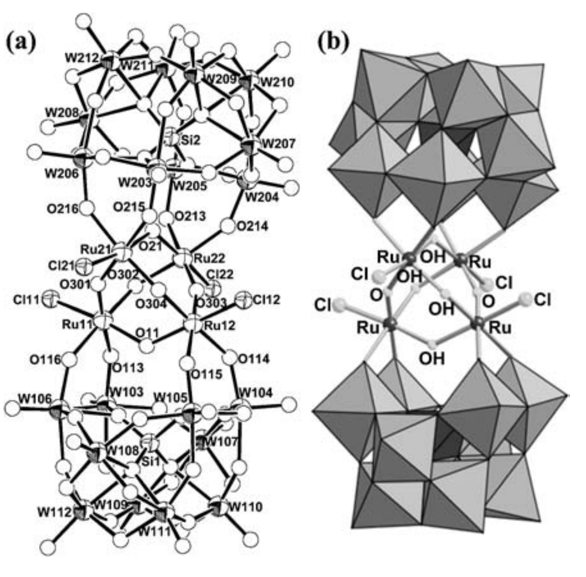

Figure 1. (a) ORTEP representation and (b) polyhedral and ball-and-stick representation of the anion part of **1**.

Table 1. Selected bond lengths and angles in **1**

Bond length/Å			
Ru11–Cl11	2.322(7)	Ru21–Cl21	2.347(8)
Ru11–O11	2.089(17)	Ru21–O21	2.131(14)
Ru11–O301	1.849(17)	Ru21–O301	1.854(17)
Ru11–O302	2.006(16)	Ru21–O304	1.959(17)
Ru11–O113	1.992(16)	Ru21–O213	2.030(17)
Ru11–O116	2.036(17)	Ru21–O216	2.049(17)
Ru12–Cl12	2.328(8)	Ru22–Cl22	2.316(8)
Ru12–O11	2.066(18)	Ru22–O21	2.031(15)
Ru12–O303	1.836(15)	Ru22–O302	2.025(17)
Ru12–O304	2.025(19)	Ru22–O303	1.724(15)
Ru12–O114	1.98(2)	Ru22–O214	2.010(18)
Ru12–O115	2.014(16)	Ru22–O215	1.994(16)
Ru11···Ru12	3.787(3)	Ru12···Ru21	3.634(2)
Ru11···Ru21	3.550(3)	Ru12···Ru22	3.497(3)
Ru11···Ru22	3.652(2)	Ru21···Ru22	3.773(3)
Bond angle/deg			
Ru11–O11–Ru12	131.4(10)	Ru12–O304–Ru21	131.6(9)
Ru11–O301–Ru21	146.9(9)	Ru12–O303–Ru22	158.4(10)
Ru11–O302–Ru22	129.9(8)	Ru21–O21–Ru22	130.0(8)

nuclear ruthenium–oxygen cluster and possessed approximately D_{2d} symmetry. Each ruthenium in **1** was in disordered octahedral environments and the coordination number was six. One axial position of the ruthenium atom was occupied by the chlorine atom (Cl ligand), and the average Ru–Cl bond length was 2.328 Å. The average Ru–O–Ru angle in **1** was 138.0° in accord with the angles (125–140°) reported for the oxo(hydroxo)-bridged cluster compounds with adamantanoid M_4O_6 cores ($M =$ Ti, Cr, Mn, Ru, In, and Ta).[8] The average Ru–O bond length and Ru···Ru distance in **1** were 1.966 and 3.649 Å, respectively, and were longer than those reported for the tetranuclear Ru^{IV} cation $[Ru_4(\mu\text{-}O)_6(H_2O)_n]^{4+}$ in aqueous solution determined by EXAFS measurements (Ru–O: 1.833 Å, Ru···Ru: 3.401 Å).[8] This is likely due to the protonation of the oxygen atoms (O11, O21, O302, and O304) in the central adamantanoid core. In the $\{\gamma\text{-}SiW_{10}Ru_2\}$ monomeric Keggin building unit of **1**, two ruthenium centers were out of the building pocket and corner sharing. Thus, each ruthenium center was coordinated to two terminal oxygen atoms of the SiW_{10} unit without direct interaction with the internal SiO_4 tetrahedron. Similar di-metal-substituted γ-Keggin POMs with the "out-of-pocket" structure have been reported.[3d,4e]

The UV–vis spectrum of an aqueous solution of **1** showed broad bands at 265 nm ($\varepsilon = 7.7 \times 10^4\,M^{-1}\,cm^{-1}$ per **1**) and 330 nm ($\varepsilon = 3.9 \times 10^4\,M^{-1}\,cm^{-1}$ per **1**), which are assignable to $O \rightarrow W$ charge-transfer (CT) bands of the γ-Keggin silicotungstate.[10] In addition to the $O \rightarrow W$ CT bands, a broad absorption band at 440 nm ($\varepsilon = 6.5 \times 10^3\,M^{-1}\,cm^{-1}$ per Ru) due to Ru^{IV} species was observed.[11] In the cyclic voltammogram of **1** (0.5 mM) in 0.2 M $HClO_4$ solution, two quasi-reversible redox waves were observed and the half-wave potentials ($E_{1/2} = (E_{pc} + E_{pa})/2$) were 0.62 and 0.47 V (vs. NHE). These $E_{1/2}$ values were in close agreement with those reported for tetranuclear Ru^{IV} cation $[Ru_4(\mu\text{-}O)_6(H_2O)_n]^{4+}$ ($E_{1/2} = 0.653$ and 0.469 V).[12] All these results suggest that the structure of **1** in the solid state is likely kept in an aqueous solution.

In summary, the novel ruthenium-containing silicotungstate with adamantanoid tetranuclear ruthenium–oxygen cluster core has been synthesized by the reaction of $K_8[\gamma\text{-}SiW_{10}O_{36}]$ with $K_2[RuCl_5(H_2O)]$ and the molecular structure was successfully determined.

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References and Notes

1 a) N. Mizuno, K. Yamaguchi, K. Kamata, *Coord. Chem. Rev.* **2005**, *249*, 1944. b) I. V. Kozhevnikov, *Catalysis by Polyoxometalates*, John Wiley & Sons, Ltd, Chichester, England, **2002**. c) Thematic Issue on Polyoxometalates: *Chemical Reviews*, ed. by C. L. Hill, American Chemical Society, Washington, DC, **1998**. d) R. Neumann, *Prog. Inorg. Chem.* **1998**, *47*, 317. e) T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* **1996**, *41*, 113. f) M. T. Pope, *Hetropoly and Isopoly Oxometalates*, Springer-Verlag, Berlin, **1983**.

2 A. Tézé, G. Hervé, *Inorganic Syntheses*, **1990**, Vol. 27, p. 85.

3 a) P. J. Domaille, R. L. Harlow, *J. Am. Chem. Soc.* **1986**, *108*, 2108. b) J. Canny, R. Thouvenot, A. Tézé, G. Hervé, M. Leparulo-Loftus, M. T. Pope, *Inorg. Chem.* **1991**, *30*, 976. c) X.-Y. Zhang, C. J. O'Connor, G. B. Jameson, M. T. Pope, *Inorg. Chem.* **1996**, *35*, 30. d) K. Wassermann, H.-J. Lunk, R. Palm, J. Fuchs, N. Steinfeldt, R. Stosser, M. T. Pope, *Inorg. Chem.* **1996**, *35*, 3273.

4 a) B. S. Bassil, M. H. Dickman, M. Reicke, U. Kortz, B. Keita, L. Nadjo, *Dalton Trans.* **2006**, 4253. b) F. Xin, M. T. Pope, *Inorg. Chem.* **1996**, *35*, 5693. c) Y. Goto, K. Kamata, K. Yamaguchi, K. Uehara, S. Hikichi, N. Mizuno, *Inorg. Chem.* **2006**, *45*, 2347. d) P. Mialane, C. Duboc, J. Marrot, E. Rivière, A. Dolbecq, F. Sécheresse, *Chem.—Eur. J.* **2006**, *12*, 1950. e) B. Botar, Y. V. Geletii, P. Kögerler, D. G. Musaev, K. Morokuma, I. A. Weinstock, C. L. Hill, *J. Am. Chem. Soc.* **2006**, *128*, 11268. f) S. Yamaguchi, Y. Kikukawa, K. Tsuchida, Y. Nakagawa, K. Uehara, K. Yamaguchi, N. Mizuno, *Inorg. Chem.* **2007**, *46*, 8502.

5 T. Naota, H. Takaya, S. Murahashi, *Chem. Rev.* **1998**, *98*, 2599.

6 a) R. Neumann, C. Abu-Gnim, *J. Am. Chem. Soc.* **1990**, *112*, 6025. b) C. Rong, M. T. Pope, *J. Am. Chem. Soc.* **1992**, *114*, 2932. c) M. Higashijima, *Chem. Lett.* **1999**, 1093. d) M. Sadakane, D. Tsukuma, M. H. Dickman, B. Bassil, U. Kortz, M. Higashijima, W. Ueda, *Dalton Trans.* **2006**, 4271. e) L.-H. Bi, E. V. Chubarova, N. H. Nsouli, M. H. Dickman, U. Kortz, B. Keita, L. Nadjo, *Inorg. Chem.* **2006**, *45*, 8575.

7 a) K. Nomiya, H. Torii, K. Nomura, Y. Sato, *J. Chem. Soc., Dalton Trans.* **2001**, 1506. b) C.-X. Yin, R. G. Finke, *Inorg. Chem.* **2005**, *44*, 4175.

8 J. R. Osman, J. A. Cryston, D. T. Richens, *Inorg. Chem.* **1998**, *37*, 1665.

9 Crystal data of **1**: $Cl_4K_2O_{79}Ru_4Si_2W_{20}$, fw 5621.46, monoclinic, space group $P2_1/c$, $a = 14.6511(6)$ Å, $b = 38.2376(17)$ Å, $c = 20.5920(9)$ Å, $\beta = 98.658(2)°$, $V = 11404.6(9)$ Å^3, $Z = 4$, $d_{calcd} = 3.274\,g\cdot cm^{-1}$, $R_1 = 0.0800$ for 9080 data ($I > 2\sigma(I)$), $wR_2 = 0.2255$ for all 25888 data.

10 A. Tézé, J. Canny, L. Gurban, R. Thouvenot, G. Hervé, *Inorg. Chem.* **1996**, *35*, 1001.

11 a) R. M. Wallace, R. C. Propst, *J. Am. Chem. Soc.* **1969**, *91*, 3779. b) R. J. H. Clark, M. L. Franks, P. C. Turtle, *J. Am. Chem. Soc.* **1977**, *99*, 2473.

12 J. Schauwers, F. Meuris, L. Heerman, W. D'Olieslager, *Electrochim. Acta* **1981**, *26*, 1065.

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