Electronic Supplementary Information for

## A discrete octahedrally shaped $[Ag_6]^{4+}$ cluster encapsulated within silicotungstate ligands

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## **Experimental Section**

**Instruments:** Liquid-state NMR spectra were recorded on JEOL JNM-EX-270. <sup>29</sup>Si (external standard: TMS), <sup>183</sup>W (external standard: 1 M Na<sub>2</sub>WO<sub>4</sub> aqueous solution), and <sup>109</sup>Ag NMR spectra (external standard: 1 M AgNO<sub>3</sub> aqueous solution) were measured at 53.5, 11.2, and 12.6 MHz, respectively. Cold-spray ionization mass (CSI-MS) spectra were recorded on JEOL JMS-T100CS. Thermogravimetric and differential thermal analyses (TG-DTA) were performed on Rigaku Thermo plus TG 8120. IR spectra were measured on Jasco FT/IR-4100 using KBr disks. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses were performed on Shimadzu ICPS-8100. Magnetic susceptibility was measured on Quantum Design MPMS-XL7 operating between 1.9 and 300 K under 1000 or 5000 Oe magnetic field. Diamagnetic corrections were applied by diamagnetism of the sample holder. The potentiometric titration of **Ag6** (0.025 mmol) was carried out in an acetone solution of ethylene carbonate (2.9 M) with a methanol solution of TBAOH (1 M) as a titrant. GC analyses were performed on Shimadzu GC-2014 with a FID detector equipped with a InertCap-1 capillary column.

**Reagents:** Silver acetate (AgOAc), silanes, TBAOH, and solvents were commercially available (from nacalai, KANTO, Aldrich, or TCI) and used as received.  $TBA_4H_4[\gamma-SiW_{10}O_{36}]\cdot H_2O$  was synthesized according to the reported procedures.<sup>10</sup>

**X-ray crystallography:** Diffraction measurements were made on a Rigaku MicroMax-007 Saturn 724 CCD detector with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å) at -120 °C. Data were collected and processed using CrystalClear<sup>S1</sup> for Windows software and HKL2000<sup>S2</sup> for Linux software. Neutral scattering factors were obtained from the standard source. In the reduction

of data, Lorentz and polarization corrections were made. The structural analysis was performed using CrystalStructure<sup>S3</sup> and Win-GX for Windows software.<sup>S4</sup> All structures were solved by SHELXS-97 (direct methods) and refined by SHELXH-97.<sup>S5</sup> The metal atoms (Si, W, and Ag) were refined anisotoropically. The oxygen atoms were refined isotoropically. The light atoms in POMs could not often be refined anisotropically due to the existence of many heavy metal atoms.<sup>S6</sup> The highly disordered solvents of crystallization (nitromethane and/or diethyl ether) in **Ag6** were omitted by the use of SQUEEZE program.<sup>S7</sup>

**BVS calculations:** BVS values were calculated by the expression for the variation of the length  $r_{ij}$  of a bond between two atoms *i* and *j* in observed crystal with valence  $V_i$ :

$$V_i = \sum_j \exp\left(\frac{r'_0 - r_{ij}}{B}\right)$$

where B is constant equal to 0.37 Å,  $r'_0$  is bond valence parameter for a given atom pair.<sup>S8</sup>

Reaction of TBA<sub>4</sub>H<sub>4</sub>[ $\gamma$ -SiW<sub>10</sub>O<sub>36</sub>] with AgOAc in the absence of 1: To an acetone solution of TBA<sub>4</sub>H<sub>4</sub>[ $\gamma$ -SiW<sub>10</sub>O<sub>36</sub>] (2.0 g, 0.58 mmol, 40 mL), AgOAc (0.29 g, 1.74 mmol, 3 equivalents with respect to TBA<sub>4</sub>H<sub>4</sub>[ $\gamma$ -SiW<sub>10</sub>O<sub>36</sub>]) were added, and the resulting solution was stirred for 3 h at room temperature (ca. 20 °C) under Ar atmosphere. Then, the white precipitates formed were filtered off, washed with acetone, and dried to afford 1.66 g of Ag4 (78% yield based on TBA<sub>4</sub>H<sub>4</sub>[ $\gamma$ -SiW<sub>10</sub>O<sub>36</sub>]). Recrystallization from a mixed solvent of acetone and DMSO gave colorless crystals of Ag4.<sup>9 29</sup>Si NMR  $\delta$  –82.0 ppm (53.5 MHz, a mixed solvent of nitromethane and acetone-*d*<sub>6</sub> (1:1, v/v), Fig. S2(a)).

**Reaction of TBA<sub>4</sub>H<sub>4</sub>[\gamma-SiW<sub>10</sub>O<sub>36</sub>] with AgOAc and 0.25 equivalents of 1: To an acetone solution of TBA<sub>4</sub>H<sub>4</sub>[\gamma-SiW<sub>10</sub>O<sub>36</sub>] (2.0 g, 0.58 mmol, 40 mL), AgOAc (0.29 g, 1.74 mmol, 3 equivalents with respect to TBA<sub>4</sub>H<sub>4</sub>[\gamma-SiW<sub>10</sub>O<sub>36</sub>]) and <b>1** (0.02 g, 0.15 mmol, 0.25 equivalents with respect to TBA<sub>4</sub>H<sub>4</sub>[ $\gamma$ -SiW<sub>10</sub>O<sub>36</sub>]) were added, and the resulting solution was stirred for 3 h at room temperature (ca. 20 °C) under Ar atmosphere. Then, the pale yellow precipitates formed were filtered off, washed with acetone, and dried to afford 1.35 g of a 1 : 1 mixture of **Ag4** and **Ag6** (62% total yield based on TBA<sub>4</sub>H<sub>4</sub>[ $\gamma$ -SiW<sub>10</sub>O<sub>36</sub>]). <sup>29</sup>Si NMR  $\delta$  –79.9 and –82.0 ppm (53.5 MHz, a mixed solvent of acetone- $d_6$  and nitromethane (1:1, v/v), intensity ratio: ca. 1 : 1, Fig. S2(b)).

Reaction of TBA<sub>4</sub>H<sub>4</sub>[ $\gamma$ -SiW<sub>10</sub>O<sub>36</sub>] with AgOAc and 0.5 equivalents of 1: To an acetone solution of TBA<sub>4</sub>H<sub>4</sub>[ $\gamma$ -SiW<sub>10</sub>O<sub>36</sub>] (2.0 g, 0.58 mmol, 40 mL), AgOAc (0.29 g, 1.74 mmol, 3 equivalents with respect to TBA<sub>4</sub>H<sub>4</sub>[ $\gamma$ -SiW<sub>10</sub>O<sub>36</sub>]) and 1 (0.04 g, 0.29 mmol, 0.5 equivalents with respect to TBA<sub>4</sub>H<sub>4</sub>[ $\gamma$ -SiW<sub>10</sub>O<sub>36</sub>]) were added, and the resulting solution was stirred for 3 h at room temperature (ca. 20 °C) under Ar atmosphere. Then, the yellow precipitates formed were filtered off, washed with acetone, and dried to afford 1.75 g of Ag6 (80% yield based on TBA<sub>4</sub>H<sub>4</sub>[ $\gamma$ -SiW<sub>10</sub>O<sub>36</sub>]). <sup>29</sup>Si NMR  $\delta$  –79.7 ppm (53.5 MHz, a mixed solvent of acetone-*d*<sub>6</sub> and nitromethane (1:1, v/v), Fig. S2(c)).

Reaction of TBA<sub>4</sub>H<sub>4</sub>[ $\gamma$ -SiW<sub>10</sub>O<sub>36</sub>] with AgOAc and 1 equivalent of 1: To an acetone solution of TBA<sub>4</sub>H<sub>4</sub>[ $\gamma$ -SiW<sub>10</sub>O<sub>36</sub>] (2.0 g, 0.58 mmol, 40 mL), AgOAc (0.29 g, 1.74 mmol, 3 equivalents with respect to TBA<sub>4</sub>H<sub>4</sub>[ $\gamma$ -SiW<sub>10</sub>O<sub>36</sub>]) and 1 (0.08 g, 0.58 mmol, 1 equivalent with respect to TBA<sub>4</sub>H<sub>4</sub>[ $\gamma$ -SiW<sub>10</sub>O<sub>36</sub>]) were added, and the resulting solution was stirred for 3 h at room temperature (ca. 20 °C) under Ar atmosphere. Then, the yellow precipitates formed were filtered off, washed with acetone, and dried to afford 1.17 g of Ag6 (53% yield based on TBA<sub>4</sub>H<sub>4</sub>[ $\gamma$ -SiW<sub>10</sub>O<sub>36</sub>]).<sup>29</sup>Si NMR  $\delta$  –79.9 ppm (53.5 MHz, a mixed solvent of acetone-*d*<sub>6</sub> and nitromethane (1:1, v/v), Fig. S2(d)).

Recrystallization and data of Ag6: The products (yellow precipitates) obtained by the reaction with 0.5 equivalents of 1 were first purified with the precipitation method (addition of 20 mL of acetone into 2 mL of a nitromethane solution of the product). Then, yellow block single crystals of Ag6 suitable for the X-ray crystallographic analysis were obtained by recrystallization from a mixed solvent of diethyl ether nitromethane (2:1)v/v). Calcd and Anal. for TBA<sub>8</sub>[Ag<sub>6</sub>(γ-H<sub>2</sub>SiW<sub>10</sub>O<sub>36</sub>)<sub>2</sub>]·5H<sub>2</sub>O: C,20.32 ; H, 4.02; N, 1.48; Si,0.74; W, 48.60; Ag, 8.55; found: C, 20.30; H, 4.07; N, 1.53; Si 0.74; W, 49.30; Ag, 8.44. IR (KBr pellet; 2000–300 cm<sup>-1</sup>): 1634, 1485, 1381, 1152, 1092, 1023, 989, 953, 893, 764, 741, 627, 553, 360, 305 cm<sup>-1</sup>. UV-vis (propylene carbonate, nm ( $\mathscr{A}$ M<sup>-1</sup>cm<sup>-1</sup>)): 276 (57000), 307 (46000). <sup>29</sup>Si NMR  $\delta$  –79.6 ppm (53.5 MHz, 2.9 M acetone- $d_6$  solution of ethylene carbonate). <sup>183</sup>W NMR  $\delta$  –115.3, –129.8, –172.8 ppm (11.2 MHz, 2.9 M acetone- $d_6$  solution of ethylene carbonate, intensity ratio: 2 : 2 : 1). <sup>109</sup>Ag NMR (12.6 MHz, 2.9 M acetone- $d_6$  solution of ethylene carbonate)  $\delta$  442 ppm. The NMR, IR, and UV-vis spectra are shown in Fig. S3, S8, and S9, respectively. CCDC 903979 contains the supplementary crystallographic data for this paper (compound **Ag6**). This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. The crystallographic and structural data are summarized in Tables S1 and S2, respectively.

**Hydrolytic oxidation of silanes:** Into a Pyrex-glass screw cap vial (volume: ca. 20 mL) were successively placed **Ag6** (1 mol%), silane (0.25 mmol), water (5.6 equivalents), and acetonitrile (1 mL). A Teflon-coated magnetic stir bar was added, and the reaction mixture was vigorously stirred (800 rpm) at 70 °C in 1 atm of air. The conversion and the product yield were determined by GC analysis. The products (silanols) were confirmed by comparison of their GC retention times, GC-MS spectra, and/or <sup>1</sup>H and <sup>13</sup>C NMR spectra with those of authentic data. The results are summarized in Table S5. Hydrolytic oxidation of dimethylphenylsilane derivatives smoothly proceeded to afford the corresponding silanols in high yields within only 1 min. The present system could be applied to sterically bulky silanes such as diphenylmethylsilane, triphenylsilane, and tribenzylsilane, giving the corresponding silanols in high yields. In the case of a double bond-containing silane, the desired unsaturated silanol was selectively obtained in 96% yield with formation of only a small amount of the over-reduced product. Compound **Ag6** could also promote the hydrolytic oxidation of a less reactive aliphatic silane.

## **Additional references**

- S1 (a) CrystalClear 1.3.6, Rigaku and Rigaku/MSC, The Woodlands, TX; (b) J. W. Pflugrath,
  Acta Crystallogr., 1999, D55, 1718.
- S2 Z. Otwinowski, W. Minor, Processing of X-ray Diffraction Data Collected in Oscillation Mode. in *Methods in Enzymology*, C. W. Carter, Jr., R. M. Sweet, Eds., Macromolecular Crystallography, Part A, Academic press, New York, 1997, Vol. 276, pp. 307–326.
- S3 CrystalStructure 3.8, Rigaku and Rigaku/MSC, The Woodlands, TX.
- S4 L. J. Farrugia, J. Appl. Crystallogr., 1999, 32, 837.
- S5 G. M. Sheldrick, SHELX97, Programs for Crystal Structure Analysis, Release 97-2, University of Göttingen, Göttingen, Germany, 1997.
- (a) M. Sadakane, M. H. Dickman, M. T. Pope, *Inorg. Chem.*, 2001, **40**, 2751; (b) C. du Peloux, A. Dolbecq, P. Mialane, J. Marrot, E. Rivière, F. Sécheresse, *Inorg. Chem.*, 2002, **41**, 7100; (c) A. J. Gaunt, L. May, D. Collison, D. Fox, *Inorg. Chem.*, 2003, **42**, 5049; (d) C. Lei, J.-G. Mao, Y.-Q. Sun, J.-L. Song, *Inorg. Chem.*, 2004, **43**, 1964; (e) A. Mazeaud, Y. Dromzee, R. Thouvenot, *Inorg. Chem.*, 2000, **39**, 4735; (f) S. Juraja, T. Vu, P. J. S. Richardt, A. M. Bond, T. J. Cardwell, J. D. Cashion, G. D. Fallon, G. Lazarev, B. Moubaraki, K. S. Murray, A. G. Wedd, *Inorg. Chem.*, 2002, **41**, 1072; (g) A. Dolbecq, E. Cadot, D. Eisner, F. Sécheresse, *Inorg. Chem.*, 1999, **38**, 4217; (h) R. Villanneau, A. Proust, F. Robert, P. Viellet, P. Gouzerh, *Inorg. Chem.*, 1999, **38**, 4981; (i) D. Volkmer, B. Bredenkötter, J. Tellenbröker, P. Kögerler, D. G. Kurth, P. Lehmann, H. Schnablegger, D. Schwahn, M. Piepenbrink, B. Krebs, *J. Am. Chem. Soc.*, 2002, **124**, 10489.
- S7 P. van der Sluis, L. A. Speck, Acta Crystallogr., 1990, A46, 194.
- S8 I. D. Brown, D. Altermatt, Acta Crystallogr., 1985, B41, 244.

Formula	$C_{128}Ag_6N_8O_{72}Si_2W_{20}\\$
Fw	7181.76
cryst syst	Monoclinic
space group	$P2_1/n$ (#14)
<i>a</i> (Å)	22.3265(2)
<i>b</i> (Å)	18.8039(3)
<i>c</i> (Å)	27.4531(4)
$\alpha$ (deg)	90
$\beta$ (deg)	94.39(0)
$\gamma(\text{deg})$	90
$V(\text{\AA}^3)$	11491.7(3)
Ζ	2
$\mu (\mathrm{mm}^{-1})$	10.532
no. of params refined	729
$R1 \ (I > 2\sigma(I))$	0.0864 (for 20010 data)
wR2	0.2753 (for all 31494 data)

Table S1. Crystallographic data of Ag6

Table S2. Selected bond lengths and angles in Ag6

Bond lengths (Å)					
Ag1-Ag2	2.7478(16)	Ag1-Ag3	2.7146(15)		
Ag1-Ag2*	2.7547(15)	Ag1-Ag3*	2.7441(15)		
Ag2-Ag3	2.7647(17)	Ag2-Ag3*	2.8579(16)		
Ag1…Ag1*	3.772				
Ag1–O5 (O <sub>Si</sub> )	2.446(9)	Ag1-O6 (O <sub>Si</sub> )	2.411(9)		
Ag2-O1 (O <sub>W</sub> )	2.295(10)	Ag2-O4* (O <sub>W</sub> )	2.272(11)		
Ag3-O2 (O <sub>W</sub> )	2.265(10)	Ag3-O3* (O <sub>W</sub> )	2.283(10)		
Angles (deg)					
Ag2-Ag1-Ag3	60.81(4)	Ag2-Ag1-Ag2*	93.45(4)		
Ag2-Ag1-Ag3*	62.72(4)	Ag3-Ag1-Ag3*	92.59(4)		
Ag3-Ag1-Ag2*	63.00(4)				
Ag1-Ag2-Ag1*	86.55(4)	Ag1-Ag2-Ag3	59.00(4)		
Ag1-Ag2-Ag3*	58.58(4)	Ag1*-Ag2-Ag3	59.63(4)		
Ag1*-Ag2-Ag3*	57.81(4)	Ag3-Ag2-Ag3*	89.13(4)		
Ag1-Ag3-Ag1*	87.41(4)	Ag1-Ag3-Ag2	60.19(4)		
Ag1-Ag3-Ag2*	59.19(4)	Ag2-Ag3-Ag2*	90.87(4)		
Ag1*-Ag3-Ag2	60.01(4)	Ag1*-Ag3-Ag2*	58.70(4)		

Complex	Ag-Ag distance (Å)	Ref.
Ag6	2.71-2.86	This work
$[Ag_{6}{S_{2}C=C(CN)_{2}_{6}}^{6-}$	3.01	14a
$[Ag_{6}{S_{2}C-N(C_{3}H_{7})_{2}}]$	3.00	14b
$[\mathrm{Ag}_{6}\mathrm{L}^{1}{}_{6}]$	2.9811-3.2071	14c
$[Ag_6(\mu-dppm)_2(\mu_3-\eta^1-C\equiv CFc)_4(CH_3OH)_2]^{2+}$	2.8978-3.2465	14d
$[Ag_{6}\{\mu_{3}\text{-}C\equiv CC\equiv C[Ru(dppe)Cp^{*}]\}_{4}(\mu\text{-}dppm)_{2}]^{2+}$	2.8104-3.0056	14e
$[Ag_6(\mu\text{-}dppm)_4 \{\mu_3\text{-}C \equiv CC \equiv C[Re(Me_2bpy)(CO)_3]\}_4]$	2.940-3.007	14f
$[Ag_6S_4]^{2^-}$	3.085	14g
$[Ag_6(\mu_3-C_5H_4NS)_6]$	2.9950-3.2830	14h
$HL^1$ = (S)-4-isopropylthiazolidine-2-thione, dppm =	$PPh_2CH_2Ph_2P$ , $FC = f$	errocenyl, dppe =
$PPh_2CH_2CH_2Ph_2P, CP^* = \eta - C_5Me_5.$		

	Table S3. Ag–Ag d	listances for the r	eported complexes	s with $[Ag_6]^{6+}$ clusters
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**Table S4.** Ag–Ag distances for the reported compounds with  $[Ag_6]^{4+}$  units

Compound	Ag-Ag distance (Å)	Ref.
Ag6	2.71-2.86	This work
$Ag_6Ge_{10}P_{12}$	2.852	12a
$Ag_6O_2$	2.757-2.863	12b
$Ag_5SiO_4 (\{[Ag_6]^{4+}(Ag^+)_4(SiO_4)_2\})$	2.704-2.862	12c
$Ag_5GeO_4 (\{[Ag_6]^{4+}(Ag^+)_4(GeO_4)_2\})$	2.74-2.84	12d

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Entry	Substrate	Time	Product	Yield (%)
1	Si-H	1 min	Si-OH	98
2	—	1 min	—————————————————————————————————————	93
3	Si-H	1 min	Si-OH	95 <sup>b</sup>
4	Si-H	1 min	Si-OH	99
5	H Si-	10 min	OH Si-	95
6	Bn₃SiH	1 h	Bn <sub>3</sub> SiOH	96
7	Et <sub>3</sub> SiH	4.5 h	Et <sub>3</sub> SiOH	93

	Table S5	5. Hydrolytic	oxidation	of various	silanes	with .	Ag6
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<sup>*a*</sup>Reaction conditions: **Ag6** (1 mol%), silane (0.25 mmol), water (5.6 equivalents with respect to silanes), acetonitrile (1 mL), 70 °C, in 1 atm of air. Yields were determined by GC analyses. Bn = benzyl; Et = ethyl. <sup>*b*</sup>Ethylmethylphenylsilanol was also formed in 3% yield.



**Fig. S1** Polyhedral and ball-and-stick representation of the anion part of **Ag4**. The  $\{WO_6\}$  and  $\{SiO_4\}$  units are shown as green octahedrons and gray tetrahedrons, respectively. Black, red, green, blue, and pink spheres indicate silver atoms, oxygen atoms of DMSO, oxygen atoms of the  $\{WO_6\}$  units  $(O_W)$ , oxygen atoms of the  $\{SiO_4\}$  units  $(O_{Si})$ , and monoprotonated oxygen atoms, respectively. DMSO molecules except for the oxygen atoms are omitted for clarity. See reference 9 in more detail.



**Fig. S2** <sup>29</sup>Si NMR spectra of products in a mixed solvent of acetone- $d_6$  and nitromethane (1:1, v/v) obtained by the reaction of TBA<sub>4</sub>H<sub>4</sub>[ $\gamma$ -SiW<sub>10</sub>O<sub>36</sub>] with 3 equivalents of AgOAc in the absence (a) or the presence of (b) 0.25, (c) 0.5, and (d) 1 equivalent(s) of **1a**.



**Fig. S3** Positive ion CSI-MS spectrum of **Ag6** in an acetone- $d_6$  solution of ethylene carbonate (2.9 M). exhibited several sets of signals centered at around m/z 3980 (**A**) and 7718 (**B**). The signal sets **A** and **B** were assignable to {TBA<sub>10</sub>[Ag<sub>6</sub>(H<sub>2</sub>SiW<sub>10</sub>O<sub>36</sub>)<sub>2</sub>]}<sup>2+</sup> and {TBA<sub>9</sub>[Ag<sub>6</sub>(H<sub>2</sub>SiW<sub>10</sub>O<sub>36</sub>)<sub>2</sub>]}<sup>+</sup>, respectively. The lines in the inset are the calculated patterns.



**Fig. S4** (a) <sup>29</sup>Si, (b) <sup>183</sup>W, and (c) <sup>109</sup>Ag NMR spectra of Ag6 in an acetone- $d_6$  solution of ethylene carbonate (2.9 M).



**Fig. S5** ORTEP representation of the anion part of  $TBA_8[Ag_6(\gamma-H_2SiW_{10}O_{36})_2]\cdot 5H_2O$  (**Ag6**); thermal ellipsoid set at 50% probability. The BVS calculations show that O22 and O23 are monoprotonated.



**Fig. S6** Potentiometric titration of **Ag6** with TBAOH. Conditions: **Ag6** (0.025 mmol), solvent (2.9 M acetone solution of ethylene carbonate), titrant (1 M methanol solution of TBAOH).



Fig. S7 Polyhedral representation of Ag6 (crystal packing). TBA cations are omitted for clarity.



Fig. S8 IR spectrum of Ag6.



Fig. S9 UV-vis spectrum of Ag6 in propylene carbonate.