SUPPORTING INFORMATION

Hexanuclear Platinum(II) Thiolate Macrocyclic Host: Charge-Transfer-Driven Inclusion of a Ag^I Ion Guest

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I. Experimental

A. Materials

Potassium tetrachloroplatinate(II) (>46.0% for Pt) and 1-dodecanethiol (99%), were obtained from Wako Pure Chemical Industries. 4-*tert*-butyltoluene (95%) was purchased from Aldrich. Acetonitrile (99%), ethanol (98%), methanol (99.5%), dichloromethane (99%) and *n*-hexane (95%) were obtained from Kanto Chemicals. Silver hexafluoroantimonate(V) (>98.0%) was obtained from TCI. Other reagents and solvents obtained from Wako Pure Chemical Industries, Kanto Chemicals, Aldrich or TCI were used as received.

B. Measurements

Optical absorption spectra were recorded using a JASCO V-670 double-beam spectrometer at 25 °C. Matrix assisted laser desorption ionization (MALDI) and electrospray ionization (ESI) mass spectra were obtained on a Shimadzu AXIMA-CFR TOF and a high-resolution Bruker micrOTOF-HS mass spectrometers, respectively. Crystal data were collected on a Bruker SMART Apex II CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The crystal structures were solved by direct methods (SHELXS-2013)¹ and refined by full-matrix least-squares methods on F^2 (SHELXL-2014)¹ with APEX II software. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and refined isotropically. ¹H NMR spectra were collected at ambient temperature on a JEOL EX-400 NMR spectrometer, and the chemical shifts (in ppm) were determined with respect to internal solvent signals.

C. Syntheses

[{Pt(SC₁₂H₂₅)₂}₆] (1): A mixture of 1-dodecanethiol (97.5 μL, 0.48 mmol), potassium tetrachloroplatinate(II) (100 mg, 0.24 mmol) and 4-*tert*-butyltoluene (10 mL) was stirred at 210 °C for 2 days in a nitrogen atmosphere. After cooling the solution, slow addition of ethanol (100 mL) resulted in a formation of orange precipitate. The solid was collected with glass filter and successively washed with methanol, ethanol, and water. Then dichloromethane was added onto the glass filter and the filtrate collected was dried. Further purification of the residue with silica gel column chromatography (100% *n*-hexane) was performed and the first yellow fraction was collected. After dryness in vacuo, yellow solid of 1 (18.7 mg, 13 % based on Pt) was obtained. Yellow plate crystals suitable for X-ray analysis were grown from solvent evaporation of *n*-hexane and ethanol. Elemental analysis: calcd (%) for 1 (C₁₄₄H₃₀₀Pt₆S₁₂): C 48.21, H 8.43, S 10.73; found: C 47.96, H 8.31, S 10.94; no nitrogen was found. MALDI-MS (m/z): 3588.6 ([M + H]⁺). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 0.86-0.90 (m, 36H), 1.24-1.36 (m, 204H), 1.43-1.50 (m, 12H), 1.63-1.76 (m, 24H), 2.55-2.63 (m, 24H).

[{Pt(SC₁₂H₂₅)₂}₆ \supset Ag](SbF₆) ([**1** \supset Ag](SbF₆)): Typically, CH₂Cl₂ solution (50 mL) of **1** (10 mg, 2.8 μmol) and MeCN solution (2 mL) of AgSbF₆ (2.0 mg, 5.8 μmol) were mixed for 5 min. To the product, after removal of solvents, was added minimum amount of CH₂Cl₂, and Bio-beads S-X3 column (CH₂Cl₂) was used for purification. The orange fraction was collected as the final product. Single crystals suitable for X-ray analysis were grown from toluene and ethanol. Elemental analysis: calcd (%) for [**1** \supset Ag](SbF₆) (C₁₄₄H₃₀₀AgF₆Pt₆S₁₂Sb): C 44.00, H 7.69, S 9.79; found C 43.85, H 7.77, S 10.00; no nitrogen was found. ESI-MS (m/z): 3694.2 ([M – SbF₆]⁺). ¹H-NMR(400 MHz, CDCl₃) δ (ppm): 0.87-0.90 (m, 36H), 1.25-1.39 (m, 204H), 1.49-1.57 (m, 12H), 1.71-1.78 (m, 24H), 2.63 (t, 12H), 2.76 (t, 12H).

D. Screening Experiments

A dichloromethane solution of $1 (5.0 \,\mu\text{M})$ was prepared by dissolving $1 (1.8 \,\text{mg})$ in CH₂Cl₂ (100 mL). For screening experiments, to 3.0 mL portions of the host solution were added various guest solutions of metal salts (3.75 mM, 5.0 molar equiv) in a 10 mm quartz cell and their absorption spectra were measured.

II. Computational Details

All the calculations were performed at density functional theory (DFT) level with TURBOMOLE package.² Geometry optimization and vibrational frequency analysis were computed at BP86^{3,4} / double- ζ plus polarization (def-SVP)⁵ level. The resolution of the identity (RI) approximation of the coulomb interaction⁶ was used for speeding up. Single-point ground-state calculation was performed at the B3LYP level^{7,8} with basis sets of split valence plus polarization quality (def2-SVP).⁹ The same exchange-correlation functional and basis sets were adopted for the subsequent calculation of electronic excitation spectrum using the time-dependent (TD) DFT method. In all calculations, default 28-electron and 60-electron relativistic effective core potentials (ECP)¹⁰ were employed for the Ag and Pt atoms, respectively. The crystallographically determined structure of $[1 \supset Ag]^+$ after replacement of SC₁₂H₂₅ with SMe groups was adopted for the initial structure of a geometry optimization calculation. The amount of the charge on the centered Ag atom was estimated using natural bond orbital (NBO) analysis.¹¹

III. Results

A. Crystal Data

 Table S1. Crystal data and structure refinement for 1.

Empirical formula	$C_{144}H_{300}Pt_6S_{12}$		
Formula weight	3587.08		
Temperature	90 K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	a = 11.7859(5) Å	$\alpha = 103.3100(6)^{\circ}$	
	b = 17.5279(8) Å	$\beta = 95.3031(6)^{\circ}$	
	c = 20.5802(9) Å	$\gamma = 105.3102(6)^{\circ}$	
Volume	3936.9(3) Å ³		
Ζ	1		
Density (calculated)	1.513 Mg/m ³		
Absorption coefficient	5.513 mm ⁻¹		
<i>F</i> (000)	1824		
Crystal size	0.22 x 0.16 x 0.15 mm ³		
Theta range for data collection	1.03 to 25.35°		
Index ranges	$-12 \le h \le 14, -21 \le k \le 18, -23 \le l \le 24$		
Reflections collected	19713		
Independent reflections	14189 [<i>R</i> (int) = 0.0172]		
Reflections with $I > 2\sigma(I)$	12166		
Completeness to theta = 26.37°	98.3 %		
Absorption correction	Empirical		
Max. and min. transmission	0.490 and 0.440		
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	14189 / 0 / 736		
Goodness-of-fit on F^2	1.089		
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0298, wR_2 = 0.0731$		
R indices (all data)	$R_1 = 0.0421, wR_2 = 0.0936$		
Largest diff. peak and hole	1.545 and -2.260 $e^{A^{-3}}$		

Table S2. Crystal data and structure refinement for [1⊃Ag](SbF₆).

Empirical formula	$C_{144}H_{300}AgF_6Pt_6S_{12}Sb$		
Formula weight	3930.70		
Temperature	90 K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	a = 15.6003(12) Å	$\alpha = 92.6717(11)^{\circ}$	
	<i>b</i> = 16.6218(13) Å	$\beta = 93.2134(11)^{\circ}$	
	c = 31.954(3) Å	$\gamma = 95.2529(10)^{\circ}$	
Volume	8226.9(11) Å ³		
Ζ	2		
Density (calculated)	1.587 Mg/m ³		
Absorption coefficient	5.560 mm^{-1}		
<i>F</i> (000)	3952		
Crystal size	0.25 x 0.14 x 0.14 mm ³		
Theta range for data collection	1.23 to 25.03°		
Index ranges	$\text{-18} \le h \le 18, \text{-19} \le k \le 18, \text{-38} \le l \le 27$		
Reflections collected	39947		
Independent reflections	28627 [$R(int) = 0.0473$]		
Reflections with $I > 2\sigma(I)$	14873		
Completeness to theta = 25.03°	98.4 %		
Absorption correction	Empirical		
Max. and min. transmission	0.510 and 0.340		
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	28627 / 1785 / 1580		
Goodness-of-fit on F^2	0.988		
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0638, wR_2 = 0.1523$		
R indices (all data)	$R_1 = 0.1504, wR_2 = 0.2109$		
Largest diff. peak and hole	2.687 and -2.410 $e^{A^{-3}}$		

B. ORTEP Drawings



Figure S1. ORTEP drawing of 1. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity.



Figure S2. ORTEP drawing of $[1 \supset Ag](SbF_6)$. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity.

C. Distances

	1	$[1 \supset Ag](SbF_6)$
Pt – Pt (adjacent) ^b	3.172 [3.089-3.230]	3.082 [3.008-3.145]
Pt - Pt (diagonal) ^b	6.342 [6.204-6.510]	6.161 [6.028-6.422]
Pt-Cent. ^{<i>a,b</i>}	3.171 [3.102-3.255]	3.080 [2.986-3.257]
S – Cent. ^{a,b}	3.814 [3.607-4.058]	3.803 [3.595-4.013]
$S - Pt^{b}$	2.320 [2.314-2.325]	2.320 [2.304-2.345]

Table S3. Summary of averaged distances (Å) in **1** and $[1 \supset Ag](SbF_6)$.

^{*a*} *Cent.* denotes the position of the gravity center in hexagonal Pt atoms (1) or the included Ag^+ ([1 \supset Ag](SbF₆)). ^{*b*} The minimum and maximum distances are given in square brackets.

D. ESI Mass Spectrum



Figure S3. Positive-ion ESI mass spectrum of $[1 \cdot Ag](SbF_6)$. The inset shows a comparison of the experimental data (top) with the calculated isotope pattern of $[{Pt(SC_{12}H_{25})_2}_6 \cdot Ag]^+$ (bottom).

E. DFT Results



Figure S4. Electron-density difference plot (0.0025 a.u.) between $[1' \supset Ag]^+$ and the simple sum of 1' and Ag⁺. Pink and aqua areas indicate the electron-rich and electron-poor regions in the formation of the inclusion compound.



Figure S5. Theoretical absorption spectrum (solid line) of $[1' \supset Ag]^+$. The lowest-energy absorption band is indicated by the two-headed pink arrow. Experimental absorption spectrum of $[1 \cdot Ag](SbF_6)$ in CH₂Cl₂ (dotted line; molar coefficient at 477 nm is $5.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) is shown for comparison.



Figure S6. The angular-momentum (*l*) projected density of states (PDOS) for the Ag atom of $[1^{\circ} \supset Ag]^{+}$. Contributions of S (l = 0), P (l = 1) and D (l = 2) states are shown in red, light green and blue, respectively. The energy scale is set relative to the HOMO energy. Large contributions of the S state are indicated by arrows, each of which corresponds to the orbitals of the LUMO (3.07 eV) and HOMO–29 (–2.33 eV), respectively. For the PDOS calculation, the Gaussian broadening with a width of 0.001 a.u. was adopted.



Figure S7. Selected molecular orbitals of $[1^{\circ} \supset Ag]^+$. The orbital and relative energies of the HOMO–29 (184a) are –10.80 and –2.33 eV, respectively. In the HOMO–29, atomic orbital contributions of Pt(*s*) (11%), Pt(*p*) (6%), Pt(*d*) (53%), S(*p*) (0%), Ag(*s*) (11%), Ag(*p*) (0%), and Ag(*d*) (17%). The hybridization of the Ag 5s and Ag 4d_v² orbitals in the HOMO–29 was seen from the bird view image. The direction vertical to the Pt hexagon through the centered Ag atom is set as the *v*-axis, which is depicted in the image.

МО	Orbital index	Orbital energy (eV) / Relative energy (eV)	% Pt (s)	% Pt (<i>p</i>)	% Pt (<i>d</i>)	% S (p)	% Ag (s)
LUMO+5	219a	-4.17 / 4.30	0	3	40	50	0
LUMO+4	218a	-4.17 / 4.30	0	3	40	50	0
LUMO+3	217a	-4.60 / 3.87	0	5	34	57	0
LUMO+2	216a	-4.60 / 3.87	0	5	34	57	0
LUMO+1	215a	-4.69 / 3.78	0	2	31	63	0
LUMO	214a	-5.40 / 3.07	3	27	18	6	36
HOMO	213a	-8.47 / 0.00	0	1	42	53	0
HOMO-1	212a	-8.68 / -0.21	0	1	26	67	0
HOMO-2	211a	-8.69 / -0.22	5	0	49	38	0
HOMO-3	210a	-8.69 / -0.22	5	0	49	38	0
HOMO-4	209a	-8.70 / -0.23	12	0	53	29	0
HOMO-5	208a	-8.70 / -0.23	12	0	53	30	0
HOMO-6	207a	-9.09 / -0.62	16	0	72	9	0
HOMO-7	206a	-9.25/ -0.78	0	2	35	53	0
HOMO-8	205a	-9.25 / -0.78	0	2	35	53	0
HOMO-9	204a	-9.34 / -0.88	3	3	40	47	0
HOMO-10	203a	-9.35 / -0.88	3	3	40	47	0
HOMO-11	202a	-9.40 / -0.93	7	17	44	40	0
HOMO-12	201a	-9.40 / -0.93	7	17	44	40	0

Table S4. Kohn-Sham orbitals, energies, and atomic orbital contributions of $[1' \supset Ag]^+$.

Table S5. Excited states, energies, oscillator strengths, and primary orbital-orbital transitions of $[1' \supset Ag]^+$. Wavelength of 350 nm or more only. The HOMO \rightarrow LUMO transition (213a \rightarrow 214a, 2.28 eV / 543 nm) with a very small oscillator strength of 2×10^{-9} is not shown in this table. The large reproducibility error between theoretical and experimental absorption spectra over 500 nm (see Figure S5) is probably due to disregard of spin-orbit couplings in the excitation calculation, as reported previously on gold clusters.¹²

Excitation index	Energy (eV) / Wavelength (nm)	Oscillator strength	Dominant transition	Nature of transition
1	2.53 / 491	0.0103	211a→214a	HOMO–2→LUMO
2	2.53 / 490	0.0102	210a→214a	HOMO–3→LUMO
3	2.58 / 481	0.0035	212a→214a	HOMO–1→LUMO
4	3.06 / 405	0.0284	213a→215a	HOMO→LUMO+1
5	3.07 / 404	0.0193	209a→215a	HOMO–4→LUMO+1
6	3.07 / 404	0.0197	208a→215a	HOMO–5→LUMO+1
7	3.08 / 403	0.0001	212a→215a	HOMO–1→LUMO+1
8	3.27 / 379	0.0006	202a→214a	HOMO–11→LUMO
9	3.28 / 378	0.0006	201a→214a	HOMO–12→LUMO
10	3.38 / 367	0.0186	212a→216a, 211a→216a	HOMO−1→LUMO+2, HOMO-2→LUMO+2
11	3.38 / 367	0.0190	212a→217a	HOMO–1→LUMO+3
12	3.44 / 360	0.0006	210a→217a, 211a→216a, 213a→215a	HOMO–3→LUMO+3, HOMO–2→LUMO+2, HOMO→LUMO+1

F. Screening Experiments



Figure S8. UV–vis absorption spectra of **1** in CH_2Cl_2 (5 μ M) before (dotted line) and after the addition of five molar equiv of various metal ions (solid lines).

References

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