

Isolation, structure and spectroscopic characterization of silver complexes of the zwitterionic thiolate Tab: $[\text{Ag}(\text{Tab})_2](\text{PF}_6)$, $\{[\text{Ag}_3(\text{tab})_4](\text{PF}_6)_3 \cdot 2\text{DMF}\}_n$, and $[\text{Ag}_{14}(\mu_6\text{-S})(\text{Tab})_{12}(\text{PPh}_3)_8](\text{PF}_6)_{12}$ (Tab = 4-(trimethylammonio)benzenethiolate)

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Abstract

Reactions of $\text{Ag}(\text{PPh}_3)_2\text{Cl}$ with equimolar TabHPF_6 (TabH = 4-(trimethylammonio)benzenethiol) under the presence of Et_3N in $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ afforded a mononuclear complex $[\text{Ag}(\text{tab})_2](\text{PF}_6)$ (**1**). Treatment of **1** with excess Na_2S in $\text{CH}_3\text{CN}/\text{DMF}$ gave rise to a unusual one-dimensional polymer $\{[\text{Ag}_3(\text{tab})_4](\text{PF}_6)_3 \cdot 2\text{DMF}\}_n$ (**2**) as a major product and a tetradecanuclear cage-like cluster $[\text{Ag}_{14}(\mu_6\text{-S})(\text{Tab})_{12}(\text{PPh}_3)_8](\text{PF}_6)_{12}$ (**3**) as a minor product. Compounds **1** and **2** were characterized by elemental analysis, IR, UV–Vis, and X-ray analysis. The Ag atom of the $[\text{Ag}(\text{Tab})_2]^+$ cation of **1** adopts a linear AgS_2 coordination geometry. Compound **2** has an one-dimensional chain structure in which the repeating $[\text{Ag}_6(\text{Tab})_8]^{6+}$ units are interconnected by four Ag–S bonds with $[\text{PF}_6]^-$ anions and DMF solvated molecules located between the polymeric chains. The structure of the $[\text{Ag}_{14}(\mu_6\text{-S})(\text{tab})_{12}(\text{PPh}_3)_8]^{12+}$ dodecation of **3** consists of a μ_6 -sulfur atom encapsulated by an $\text{Ag}_{14}\text{S}_{12}$ cage. The luminescence properties of **1** and **2** in solution and in the solid state at room temperature are also reported.

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1. Introduction

Over the past decades, there has been considerable interest in the coordination chemistry of silver complexes of organic thiolates due to their structure diversity [1–6] and potential application as precursors for materials [7–10], antimicrobial drugs [11], and models for the active site of metallothioneins [12,13]. However, the chemistry of silver complexes of the zwitterionic organic thiolates is less explored and as a matter of fact, only several compounds have been structurally determined so far [14–16].

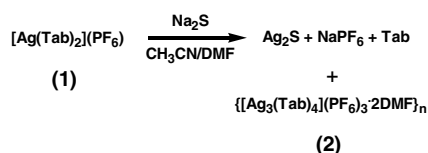
For example, treatment of $[\text{NET}_4][\text{AgCl}_2]$ with 2-mercaptoethylamine hydrogen chloride in DMF gave rise to an 1D chain polymer $[\{\text{Ag}_8(\mu_4\text{-SC}_2\text{H}_4\text{NH}_3)_6\text{Cl}_2\}\text{Cl}_2]_n$. In the case of TabHPF_6 (TabH = 4-(trimethylammonio)benzenethiol) [17], there are several papers which reported the utilization of this ligand [18] and only one compound $[(\text{PPh}_3)\text{Au}(\text{Tab})](\text{PF}_6)$ was structurally determined [19]. Actually the chemistry of this zwitterionic thiolate with other transition metals is virtually unknown. In this regard, we carried out the reaction of TabHPF_6 with $\text{Ag}(\text{PPh}_3)_2\text{Cl}$ and successfully isolated three novel Ag/Tab complexes: $[\text{Ag}(\text{tab})_2](\text{PF}_6)$ (**1**), $\{[\text{Ag}_3(\text{tab})_4](\text{PF}_6)_3 \cdot 2\text{DMF}\}_n$ (**2**), and $[\text{Ag}_{14}(\mu_6\text{-S})(\text{tab})_{12}(\text{PPh}_3)_8](\text{PF}_6)_{12}$ (**3**) (minor product). Compounds **1** and **2** exhibited the luminescence properties both in solution and in

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Table 1
Selected bond distances (Å) and angles (°) for **1**, **2** and **3**

1			
Ag(1)–S(1)	2.391(2)	Ag(2)–S(2)	2.379(3)
C(1)–S(1)–Ag(1)	105.2(3)	C(10)–S(2)–Ag(2)	105.8(4)
S(1)–Ag(1)–S(1')	180	S(2)–Ag(2)–S(2')	180
2			
Ag(1)–S(1)	2.483(4)	Ag(1)–S(2)	2.592(4)
Ag(1)–S(4)	2.538(4)	Ag(2)–S(3)	2.561(3)
Ag(2)–S(2)	2.514(4)	Ag(2)–S(1'')	2.524(4)
Ag(3)–S(4)	2.481(4)	Ag(3)–S(3)	2.488(4)
Ag(3)–S(2')	2.577(4)	Ag(2)···Ag(3)	3.207(2)
Ag(1)···Ag(3)	3.560(2)	Ag(3)···Ag(3')	3.896(2)
S(1)–Ag(1)–S(2)	115.61(12)	S(1)–Ag(1)–S(4)	125.53(13)
S(2)–Ag(1)–S(4)	105.06(11)	S(2)–Ag(2)–S(3)	116.81(12)
S(2)–Ag(2)–S(1'')	132.45(12)	S(3)–Ag(2)–S(1'')	107.24(12)
S(3)–Ag(3)–S(4)	120.45(13)	S(3)–Ag(3)–S(2')	114.93(12)
S(4)–Ag(3)–S(2')	122.79(12)	Ag(1)–S(2)–Ag(2)	108.82(12)
Ag(2)–S(2)–Ag(3')	115.67(13)	Ag(1)–S(2)–Ag(3')	115.79(13)
Ag(3)–S(3)–Ag(2)	78.86(10)	Ag(1)–S(4)–Ag(3)	90.33(12)
Ag(1)–S(1)–Ag(2'')	99.5(1)		
3			
Ag(1)–S(1)	2.6625(12)	Ag(1)–S(1a)	2.663(4)
Ag(1)–S(1b)	2.663(5)	Ag(2)–S(2)	2.937(2)
Ag(2)–S(1)	2.423(5)	Ag(2)–S(1g)	2.423(5)
Ag(1)–P(1)	2.475(3)		
S(1)–Ag(1)–P(1)	119.00(12)	S(1)–Ag(1)–S(1a)	98.48(9)
S(1)–Ag(1)–S(1b)	98.48(12)	P(1)–Ag(1)–S(1a)	119.00(11)
P(1)–Ag(1)–S(1b)	119.00(9)	S(1a)–Ag(1)–S(1b)	98.5(1)
S(1)–Ag(2)–S(2)	94.96(11)	S(1)–Ag(2)–S(1g)	170.1(2)
S(2)–Ag(2)–S(1g)	94.96(11)	Ag(1)–S(1)–Ag(2)	92.94(11)



Scheme 2.

anions. Fig. 3 presents the perspective view of a part of the polymeric cationic chain of **2**. Each $[\text{Ag}_6(\text{Tab})_8]^{6+}$ has a saddle-shaped Ag_6S_6 core structure with a crystallographic symmetry center on the midpoint of Ag(3) and Ag(3'). The core structure consists of two eight-membered Ag_4S_4 boat-like rings ($\text{Ag}(1)\text{S}(2)\text{Ag}(3')\text{S}(3')\text{Ag}(2')\text{S}(2')\text{Ag}(3)\text{S}(4)$ and $\text{Ag}(2)\text{S}(3)\text{Ag}(3)\text{S}(2')\text{Ag}(1')\text{S}(4')\text{Ag}(3')\text{S}(2)$), which share the same boat-bottom plane ($\text{Ag}(3)\text{S}(2')\text{Ag}(3')\text{S}(2)$). In the Ag_6S_6 core, either Ag(1) or Ag(1') atom is coordinated by a μ_3 -S and two μ -S atoms, showing a pyramidalized Y-shape coordination geometry. Such a coordination is uncommon in the Ag(I) complexes [24]. The Ag(1) atom is displaced 0.55 Å from the trigonal plane of S(1), S(2), and S(4). On the other hand, the Ag(2) and Ag(3) atoms show typical trigonal planar geometry. As shown in Table 1, the average Ag–S bond length of

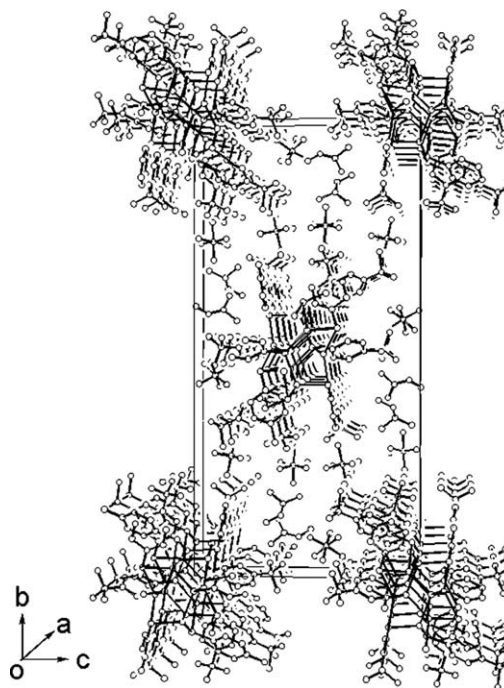


Fig. 2. Cell packing diagrams of **2** looking down the *a*-axis. Hydrogen atoms are omitted for clarity.

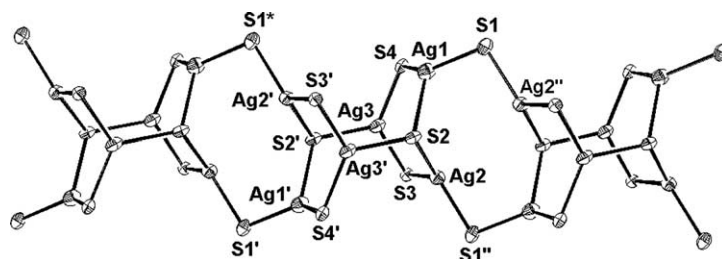


Fig. 3. Perspective view of a part of the polymeric cationic chain in **2** with 50% thermal ellipsoids. The $C_6H_4NMe_3$ groups are omitted for clarity.

2.529 Å is not unusual as compared with the structures containing three-coordinated Ag(I) such as $[PPh_4]_2[Ag_4(SCH_2C_6H_4CH_2S)_3]$ (2.505 Å) and $[PPh_4]_3[Ag_9(SCH_2CH_2S)_6]$ (2.579 Å) [25,26]. The Ag...Ag contacts range from 3.207(2) to 3.896(2) Å, which fall into two categories. The Ag(2)...Ag(3) contact of 3.207(2) Å is shorter than the sum of the van der Waals radii of two Ag atoms (3.44 Å), and may suggest they are related by so-called agentophilicity [27]. The Ag(2)...Ag(3) and Ag(3)...Ag(3a) separations, 3.560(2) and 3.896(2) Å, may be assumed to be non-bonding and may be involved in very weak interactions.

Compound **3** crystallizes in the cubic space group $Im\bar{3}$ and the asymmetric unit of **3** contains 24th of $[Ag_{14}(\mu_6-S)(tab)_{12}(PPh_3)_8]^{12+}$ dodecation, one-half of PF_6^- anion, and one-half of MeCN solvated molecule. As shown in Fig. 4, the cluster framework of the dodecation has an $Ag_{14}S_{12}$ cage that is composed of Ag_8 cube, Ag_6 octahedron, and an S_{12} icosahedron centred around a μ_6 -sulfur atoms. The structure of the $Ag_{14}S_{12}$ cage closely resembles that of neutral phenyl thiolate analogue $[Ag_{14}(\mu_6-S)(SPh)_{12}(PPh_3)_8]$ [28]. Each Ag atom in Ag_8 cube of **3** adopts a distorted tetrahedral geometry while that in Ag_6 octahedron has a trigonal geometry. As presented in Table 1, the average Ag(octa)- μ_6 -S, Ag(octa)-S, Ag(cube)-S, and Ag-P bond lengths, 2.936, 2.426, 2.6625(12), and 2.475(3) Å, are somewhat longer

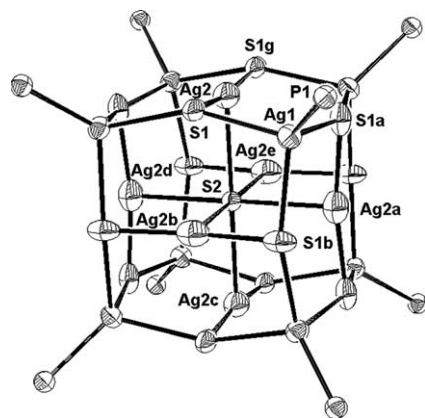


Fig. 4. Perspective view of the $[Ag_{14}(\mu_6-S)(tab)_{12}(PPh_3)_8]^{12+}$ dodecation of **3** with 50% thermal ellipsoids. The $C_6H_4NMe_3$ and phenyl groups are omitted for clarity.

than those of the corresponding ones in $[Ag_{14}(\mu_6-S)(SPh)_{12}(PPh_3)_8]$.

2.3. Spectral aspects of **1** and **2**

Solids **1** and **2** are relatively stable towards oxygen and moisture. They are soluble in CH_3CN , DMSO, and DMF but insoluble in benzene, CH_2Cl_2 , and $CHCl_3$. The elemental analysis of **1** and **2** were consistent with their chemical formula. In the IR spectra of **1** and **2**, characteristic bands due to vibrations of Ph (1485, 1126 and 1006 cm^{-1}) and PF_6^- (837 and 559 cm^{-1}) were observed. The 1H NMR spectrum of **1** and **2** in $(CD_3)_2SO$ at room temperature showed a multiplet for Ph groups at 7.43–7.48 ppm and a single peak related to NMe_3 protons at 3.34 ppm.

As shown in Fig. 5, complex **1** or **2** in MeCN shows a strong absorption at 293 nm (**1**) or 296 nm (**2**) and a long absorption tail to ca. 400 nm. Since the absorption spectrum of the corresponding free ligand Tab (prepared from reaction of TabH PF_6 with excess Et_3N in MeCN) in MeOH has a broad absorption band at 283 nm, the peaks at 293 nm (**1**) and 296 nm (**2**) observed in the spectra of **1** and **2** in MeCN are red-shifted, and are

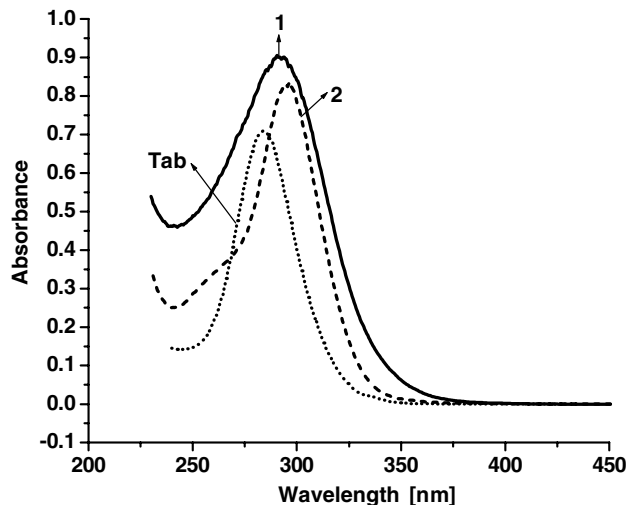


Fig. 5. Absorption spectra of **1** (solid line) and **2** (short dashed line) in MeCN along with the free Tab ligand (short dotted line) in MeOH with a 1 mm optical length.

probably originated from intraligand transitions. Interestingly, compounds **1** and **2** exhibited luminescence in solution and in solid state at ambient temperature, respectively. As shown in Fig. 6, excitation of **1** at $\lambda_{\text{ex}} > 320$ nm resulted in an intense emission at 420 nm in solution, while that of **2** at $\lambda_{\text{ex}} > 310$ nm gave rise to a similar band at 443 nm. On the other hand, excitation of **1** in the solid state at 390 nm resulted in broad emission bands at 442 and 533 nm while that of **2** at 395 nm gave a broad emission band centered at 535 nm (Fig. 7). However, the free ligand Tab is not emissive both in MeOH and in the solid state at ambient temperature. As mentioned above, a set of gold/thiolate complexes $[(n\text{-Bu})_4\text{N}][\text{Au}(\text{SC}_6\text{H}_4\text{R})]$ (R = *o*-Me, *o*-Cl, *m*-Cl) have a similar linear AuS_2 structure to that of **1**. These complexes were confirmed to possess luminescence in the

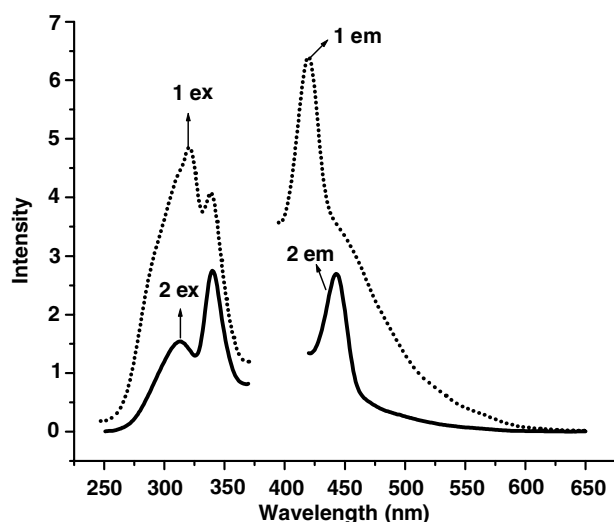


Fig. 6. Excitation and emission spectra of complex **1** (solid line) and **2** (dashed line) in MeCN at ambient temperature.

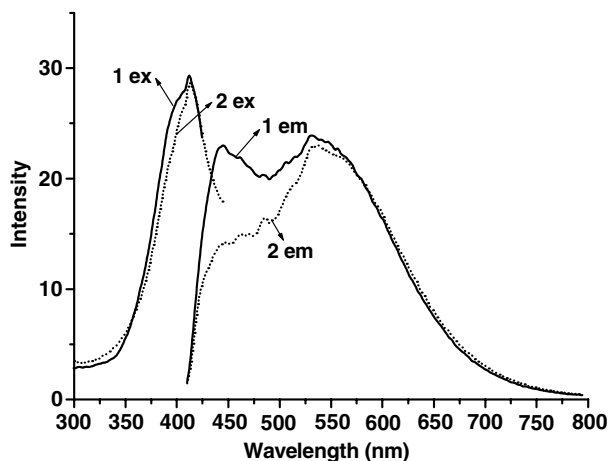


Fig. 7. Excitation and emission spectra of complex **1** (solid line) and **2** (dashed line) in the solid state at ambient temperature.

solid state derived from metal-to-ligand charge transfer (MLCT) or a ligand-centered (LC) transition [21,29]. Therefore, the possible origins of emissions of **1** and **2** may be tentatively assumed to be MLCT from silver (4d) to ligand (π^*) or LC transition from S (non-bonding 3p) to benzene ring (π^*) of the Tab ligand [21,30,31], though the metal-centered transition arising from the silver–silver contacts could not be ruled out for compound **2**.

3. Experimental

3.1. General

TabHPF₆ was prepared according to the literature method [32]. Other reagents were obtained from commercial sources and used as received. All solvents were predried over activated molecular sieves and refluxed over the appropriate drying agents under argon. IR spectra (KBr disc) were recorded on a Nicolet MagNA-IR 550 spectrophotometer. Elemental analyses for C, H, and N were performed on an EA1110 CHNS elemental analyzer. ¹H NMR spectra were recorded at ambient temperature on a Varian UNITYplus-400 spectrometer. ¹H NMR chemical shifts were referenced to the (CD₃)₂SO signal. UV–Vis spectra were measured on HITACHI U-2810 spectrophotometer. The photoluminescent spectra were performed by HITACHI F-2500 spectrofluorometer.

3.2. Syntheses

3.2.1. Preparation of **1**

To a suspension containing TabHPF₆ (66 mg, 0.21 mmol) in CH₃OH (5 ml) was added Et₃N (0.25 ml). The resulting colorless solution was then treated with a solution of Ag(PPh₃)₂Cl (133 mg, 0.20 mmol) in CH₂Cl₂ (10 ml). The mixture was refluxed on an oil bath for 0.5 h and a white precipitate was formed. After filtration, the filtrate was cooled down to 5 °C to form colorless crystals of [Ag(PPh₃)₄](PF₆). Yield: 121 mg (93.1% based on Ag). Anal. Calc. for C₇₂H₆₀AgF₆P₅: C, 66.41; H, 4.61. Found: C, 66.89; H, 4.53%. IR (KBr disc): 1477 (m), 1435 (s), 1091 (m), 837 (s), 744 (m), 694 (s), 555 (m), 509 (s) cm⁻¹. On the other hand, the white solid was redissolved in CH₃CN (5 ml) to give a colorless solution. Diethyl ether (10 ml) was allowed to diffuse into the CH₃CN solution to afford colorless plates of [Ag(Tab)₂](PF₆) (**1**), which were collected by filtration and washed with CH₂Cl₂/Et₂O (1:4) and dried in vacuo. Yield: 51.1 mg (87.0% based on Ag). Anal. Calc. for C₁₈H₂₆AgF₆N₂PS₂: C, 36.80; H, 4.43; N, 4.77. Found: C, 36.93; H, 4.21; N, 4.56%. IR (KBr disc): 1485 (m), 1126 (w), 1006 (w), 837 (s), 559 (m) cm⁻¹. UV–Vis (CH₃CN, λ_{max} (nm (ϵ M⁻¹ cm⁻¹)): 293 (8400). ¹H

NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$): δ 7.43–7.48 (m, 4H, Ph), 3.34 (s, 9H, NMe_3).

3.2.2. Preparation of **2** and **3**

Addition of Na_2S (4 mg, 0.05 mmol) into the solution of **1** (469 mg, 0.8 mmol) in $\text{CH}_3\text{CN}/\text{DMF}$ (10 ml, v/v = 9:1) gave some insoluble black precipitate. After filtration, Et_2O (10 ml) was allowed to diffuse into the filtrate. After standing it at ambient temperature for several days, long colorless column crystals of $\{[\text{Ag}_3(\text{Tab})_4](\text{PF}_6)_3 \cdot 2\text{DMF}\}_n$ (**2**) coupled with several colorless plates of $[\text{Ag}_{14}(\mu_6\text{-S})(\text{tab})_{12}(\text{PPh}_3)_8](\text{PF}_6)_{12}$ (**3** · $12\text{CH}_3\text{CN}$) were formed, which were separated mechanically under the microscope. Yield for **2**: 240 mg (75% based on Ag). Anal. Calc. for $\text{C}_{42}\text{H}_{66}\text{Ag}_3\text{F}_{18}\text{N}_6\text{O}_2\text{P}_3\text{S}_4$: C, 32.03; H, 4.19; N, 5.34. Found: C, 32.19; H, 4.30; N, 5.63%. IR (KBr disc): 1485 (m), 1126 (w), 1006 (w), 837 (s), 559 (m) cm^{-1} . UV–Vis (CH_3CN , λ_{max} (nm (ϵ $\text{M}^{-1}\text{cm}^{-1}$)): 296 (26 800). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$): δ 7.43–7.48 (m, 4H, Ph), 3.34 (s, 9H, NMe_3). The identity of **3** · $12\text{CH}_3\text{CN}$ was confirmed directly by an X-ray analysis.

3.2.3. X-ray structure determination

All measurements were made on a Rigaku Mercury CCD X-ray diffractometer (3 kW, sealed tube) by using graphite monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71070$ Å). Crystals of **1** suitable to X-ray analysis were obtained from recrystallization in CH_3CN while **2** and **3** · $12\text{CH}_3\text{CN}$ were obtained directly from the above

preparation. A colorless plate crystal of **1** with dimensions $0.45 \times 0.40 \times 0.10$ mm, a colorless long column crystal of **2** with dimensions of $0.20 \times 0.45 \times 0.15$ mm, and a colorless plate of **3** · $12\text{CH}_3\text{CN}$ with dimensions of $0.35 \times 0.20 \times 0.20$ mm were mounted at the top of a glass fiber, and cooled at 193 K in a liquid nitrogen stream. Diffraction data were collected at ω mode with a detector to crystal distance of 45 mm (**1**), 55 mm (**2**), and 55 mm (**3** · $12\text{CH}_3\text{CN}$), respectively. Indexing was performed from six images each of which was exposed for 15 s (**1** and **2**) and 20 s (**3** · $12\text{CH}_3\text{CN}$). Cell parameters were refined by using the program CRYSTALCLEAR (Rigaku and MSc, Ver. 1.3, 2001) on all observed reflections between θ of 1.5° and 31.5° (**1**), 3° and 27.5° (**2**), and 1.6° and 30.5° (**3** · $12\text{CH}_3\text{CN}$). A total of 720 (**1**, **2** and **3** · $12\text{CH}_3\text{CN}$) oscillation images were collected in the range $1.77^\circ < 2\theta < 62.6^\circ$ for **1** and $1.87^\circ < 2\theta < 55^\circ$ for **2**, and $1.92^\circ < 2\theta < 61.5^\circ$ for **3** · $12\text{CH}_3\text{CN}$. The collected data were reduced by using the program CRYSTALSTRUCTURE (Rigaku and MSC, Ver. 3.16, 2003), and an absorption correction (Multi-Scan) was applied which resulted in transmission factors ranging from 0.596 to 0.889 for **1** and from 0.734 to 0.819 for **2**, and 0.759 to 0.795 for **3** · $12\text{CH}_3\text{CN}$. The data were also corrected for Lorentz and polarization effects.

The structures of **1**, **2**, and **3** · $12\text{CH}_3\text{CN}$ were solved by heavy-atom Patterson methods (**1**) [33], and direct methods (**2**, and **3** · $12\text{CH}_3\text{CN}$) [34], and were refined by full-matrix least-squares on F [35]. Non-hydrogen atoms

Table 2
Crystallographic data for **1**, **2**, and **3**

Molecular formula	$\text{C}_{18}\text{H}_{26}\text{AgF}_6\text{N}_2\text{PS}_2$	$\text{C}_{42}\text{H}_{66}\text{Ag}_3\text{F}_{18}\text{N}_6\text{O}_2\text{P}_3\text{S}_4$	$\text{C}_{276}\text{H}_{312}\text{Ag}_{14}\text{F}_{72}\text{N}_{24}\text{P}_{20}\text{S}_{13}$
Formula weight	587.39	1573.81	7843.7
Crystal system	Monoclinic	Monoclinic	Cubic
Space group	$C2/c$	$P1/c$	$Im\bar{3}$
a (Å)	33.23(1)	8.7364(5)	24.9371(10)
b (Å)	10.158(4)	36.575(2)	
c (Å)	14.316(6)	18.1407(12)	
β ($^\circ$)	106.736(4)	95.073(3)	
V (Å ³)	4627.5(32)	5773.9(6)	15507.4(11)
Z	8	4	2
T (K)	193	193	193
D_{calc} (g cm^{-3})	1.686	1.811	1.680
λ (Mo $\text{K}\alpha$) (Å)	0.71070	0.71070	0.71070
μ (cm^{-1})	11.76	13.35	11.51
$2\theta_{\text{max}}$ ($^\circ$)	62.6	55.0	61.5
Total reflections	20323	38659	59186
Unique reflections (R_{int})	6737 (0.036)	12407 (0.050)	4140 (0.058)
Number of observations	2330 ($I > 3.00\sigma(I)$)	4491 ($I > 2.00\sigma(I)$)	1296 ($I > 2.00\sigma(I)$)
Number of parameters	269	414	118
R^a	0.057	0.061	0.062
R_w^b	0.065	0.065	0.071
Goodness-of-fit ^c	1.068	1.198	1.173
$\Delta\rho_{\text{max}}$ ($\text{e } \text{Å}^{-3}$)	1.38	1.38	1.85
$\Delta\rho_{\text{min}}$ ($\text{e } \text{Å}^{-3}$)	−0.81	−0.99	−1.13

$$^a R = \sum |F_o| - |F_c| / \sum |F_o|.$$

$$^b R_w = \left\{ \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 \right\}^{1/2}.$$

$$^c \text{GOF} = \left\{ \sum w(|F_o| - |F_c|)^2 / (M - N) \right\}^{1/2}, \text{ where } M \text{ is number of reflections and } N \text{ is number of parameters.}$$

except for the F atoms in **1**, those of PF_6^- , DMF, and $\text{C}_6\text{H}_4\text{NMe}_3$ groups in **2**, and those of PF_6^- , CH_3CN , phenyl groups, and $\text{C}_6\text{H}_4\text{NMe}_3$ groups in $\mathbf{3} \cdot 12\text{CH}_3\text{CN}$, were refined anisotropically, and hydrogen atoms were put on the calculated positions and refined in the final structure factor refinement. Neutral atom scattering factors were taken from Cromer and Waber [36]. Anomalous dispersion effects were included in F_{calc} [37]. All calculations were performed on a Dell workstation using the CrystalStructure crystallographic software package (Rigaku and MSC, Ver. 3.16, 2003) (Table 2).

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with Cambridge Crystallographic Data Centre, CCDC reference numbers 213942 (**1**), 213943 (**2**), and 213944 ($\mathbf{3} \cdot 12\text{CH}_3\text{CN}$). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1E2, UK (fax: +44-1223-336033; deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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