Solid-State Reactions of AgAc with TabHPF$_6$ at Room Temperature − Isolation and Structural Characterisation of an Unusual Octadecanuclear Silver Thiolate Cluster [Ag$_9$(Tab)$_8$(MeCN)$_8$]$_2$(PF$_6$)$_{18}$·4MeCN [Tab = 4-(trimethylammonio)benzenethiolate]

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The room-temperature solid-state reaction of silver acetate with TabHPF$_6$ [Tab = 4-(trimethylammonio)benzenethiolate] followed by recrystallization from MeCN afforded a unique octadecanuclear silver thiolate complex [Ag$_9$(Tab)$_8$(MeCN)$_8$]$_2$(PF$_6$)$_{18}$·4MeCN (**1**). An X-ray analysis of **1** revealed that the structure of [Ag$_9$(Tab)$_8$(MeCN)$_8$]$_2^{18+}$ contains an unprecedented tubular motif in which one central saddle-shaped Ag$_6$S$_6$ fragment and two identical Ag$_5$S$_6$ fragments are interconnected by a pair of Ag atoms and four Ag–S bonds. The solid-state product was assumed to be [Ag$_9$(Tab)$_8$]$_2$(PF$_6$)$_{18}$ and might have the Ag$_{18}$S$_{16}$ core structure of **1** based on elemental analysis, IR spectroscopy, ^{1}H NMR spectroscopy, luminescence spectra, XRD and TGA measurements.

Introduction

In recent years, silver thiolate complexes have been of intense interest due to their unique structures,[1−3] their relations to metallothioneins[4,5] and their potential applications in advanced materials [6−9] and antimicrobial drugs.[10] Usually, such complexes are prepared through routine solution reactions. Very few have been reported to have been prepared by solid-state reactions of silver salts with thiolates, especially at room temperature. On the other hand, we have been interested recently in the preparation of silver sulfide clusters from thiometallates with silver salts in the solid state.[11] In these reactions, the solid-state product must be extracted using certain solvents in order for structural characterisation to be carried out.[11a] One question may then arise: Does the solid-state product interact with solvent molecules when it is extracted? This is likely to be true because in the structure of the solid-state products, there are a number of metal atoms with vacant coordination sites which may be further coordinated by solvent molecules bearing donor atoms. However, isolation of such solvent-ligated products is difficult due to their instability arising from the weak coordination between the metal atoms and solvent molecules. In our continuing exploitation of solid-state syntheses of new metal thiolate clusters, we found that a zwitterionic thiolate TabHPF$_6$ [Tab = 4-(trimethylammonio)benzenethiolate][12] readily reacts with AgAc in the solid state at room temperature. When the resultant solid-state product was extracted with acentonitrile, an intriguing octadecanuclear silver thiolate cluster [Ag$_9$(Tab)$_8$(MeCN)$_8$]$_2$(PF$_6$)$_{18}$·4MeCN (**1**) was formed in high yield. This represents an interesting example of the isolation of the solid-state product having solvent molecules coordinated and solvated. Herein we report its synthesis and structural characterisation.

Results and Discussion

Silver acetate (argenteous powder) and TabHPF$_6$ (white powder) were mixed in a molar ratio of 1:1 and firmly ground in an agate mortar at ambient temperature for about 0.5 h. During grinding, a strong smell of acetic acid was apparent while the colour of the mixture gradually became yellow. The liberation of the volatile acetic acid vapour might be the driving force for this solid-state reaction. The IR spectrum of the yellow powder showed the disappearance of the stretching vibration of the S−H group of TabHPF$_6$ at 2592 cm^{-1},[2f] implying completeness of the reaction. As shown in Scheme 1, the reaction yielded 1 equiv.

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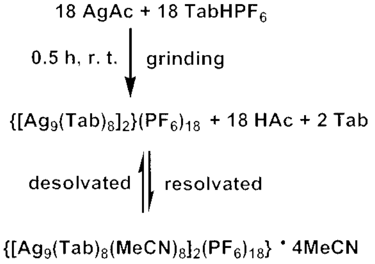
of acetic acid and 1/9th of an equivalent of the zwitterionic Tab ligand which is very soluble in methanol. Consequently, we thoroughly washed the powder with MeOH and Et_2O and then dried the product in vacuo for 1 h to form a yellow solid **1a**. Subsequent extraction of **1a** with MeCN, followed by diffusion of Et_2O into the extract gave rise to colourless crystals of $[Ag_9(Tab)_8(MeCN)_8]_2(PF_6)_{18}\cdot 4MeCN$ (**1**) in 95% yield; the elemental analysis of **1** corresponds to this formula. The IR spectrum of **1** shows a C=N stretching vibration for MeCN at 2262 cm^{-1} and two strong characteristic peaks arising from PF_6 at 841 and 559 cm^{-1}. The ^1H NMR spectrum of **1** in $[D_6]DMSO$ exhibits a single signal at $\delta = 2.07$ ppm for protons of the MeCN molecules, a singlet at $\delta = 3.34$ ppm for the NMe_3 groups and multiplets in the $\delta = 7.43-7.48$ ppm region for the phenyl groups. The identity of **1** was finally confirmed by a single-crystal X-ray diffraction study.



Scheme 1

Compound **1** crystallises in the triclinic space group $P\bar{1}$ and the asymmetric unit contains one-half of the discrete $[Ag_9(Tab)_8(MeCN)_8]_2^{18+}$ cation, ten $[PF_6]^-$ anions (two of them having an occupancy of 0.5) and two MeCN solvate molecules. Figure 1 shows the packing diagram of **1** in the unit cell. The $[Ag_9(Tab)_8(MeCN)_8]_2^{18+}$ cations are parallel to each other along the *c* axis. The associated $[PF_6]^-$ anions are located between the two tubular octadecacations. Except for the electrostatic forces between the octadecacations and the $[PF_6]^-$ anions, there are no other apparent interactions between the MeCN solvent molecules and the octadecacations or the $[PF_6]^-$ anions.

Figure 2 shows a perspective view of the $[Ag_9(Tab)_8(MeCN)_8]_2^{18+}$ ion while Figure 3 represents a side-view of the tubular structure of the octadecacation of **1**. Table 1 lists selected bond lengths and angles of **1**. Being a crystallographic centre of symmetry on the midpoint of Ag(1) and Ag(1′), the octadecacation of **1** contains 18 Ag atoms, 16 Tab moieties and 16 coordinated MeCN molecules. The $Ag_{18}S_{16}$ core of the octadecacation may be visualised as a long tubular structure which is composed of one central saddle-shaped Ag_6S_6 fragment and two identical Ag_5S_6 fragments bridged by a pair of Ag [Ag(3) and Ag(3′)] atoms and four Ag−S bonds [Ag(5)−S(5), Ag(4)−S(2), Ag(5′)−S(5′) and Ag(4′)−S(2′)]. The Ag_6S_6 fragment consists of two six-membered Ag_3S_3 rings, Ag(5)S(1′)Ag(1′)S(2′)Ag(2′)S(4′) and Ag(5′)S(1)Ag(1)S(2)Ag(2)S(4), which are held together by the Ag(1)−S(4′) and Ag(1′)−S(4) bonds. Each Ag_5S_5 fragment is composed of one six-membered Ag(9)S(7)Ag(7)S(3′)Ag(8)S(8) [or Ag(9′)S(7′)Ag(7′)S(3)Ag(8′)S(8′)] ring and one eight-membered Ag(9)S(7)Ag(7)S(6)Ag(6)S(5)Ag(4)S(8) [or Ag(9′)S(7′)Ag(7′)S(6′)Ag(6′)S(5′)Ag(4′)S(8′)] ring, sharing a group of Ag(9), S(7), Ag(7) and S(8) [or Ag(9′), S(7′), Ag(7′) and S(8′)] atoms. It is noteworthy that the coordination geometry of the 18 Ag atoms can be classified into three groups: distorted tetrahedral [Ag(1), Ag(1′), Ag(4), Ag(4′), Ag(5) and Ag(5′)], pyramidalised Y-shape [Ag(8) and Ag(8)] and trigonal planar [Ag(2), Ag(2′), Ag(3), Ag(3′), Ag(6), Ag(6′), Ag(7) Ag(7′) Ag(9) and Ag(9′)]. As can be seen in Table 1, most Ag···Ag contacts [3.011(3)−3.426(3) Å] are similar to those found in $\{[Ag_3(Tab)_4](PF_6)_3\cdot 2DMF\}_n$ [3.207(2) Å],[2f] but shorter than the sum of the van der Waals radii of two Ag atoms (3.44 Å), implying the possible existence of the silver−silver interactions.[13] Other relatively longer Ag···Ag separations such as Ag(3)···Ag(7′) = 3.667(3) Å and Ag(2)···Ag(8) = 3.758(3) Å may constitute weak nonbonding interactions. The sixteen sulfur atoms show doubly bridging [S(6), S(6′), S(7), S(7′)] and triply bridging [S(1) to S(5), S(1′) to S(5′), S(8), S(8′)] modes. The observed trend in the Ag−S bond lengths varying from 2.397(5) to 2.654(5) Å correlates with the coordination geometries of the Ag centres. The average Ag−S bond length of 2.512 Å is not unusual when compared with structures containing three-coordinate Ag^I such as $\{[Ag_3(Tab)_4](PF_6)_3\cdot 2DMF\}_n$ (2.529 Å),[2f] $[PPh_4]_2[Ag_4(SCH_2C_6H_4CH_2S)_3]$ (2.505 Å)[14] and $[PPh_4]_3[Ag_9(SCH_2CH_2S)_6]$ (2.579 Å).[15] Interestingly, as shown in Figure 1, except for Ag(7) and Ag(7′), the other sixteen Ag atoms are coordinated by sixteen MeCN molecules in an ordered way: 5 each on the right or left side and 3 each behind or before the tubular structure. Judging from the Ag−N bond lengths listed in Table 1, however, the strengths of the interactions between the Ag atoms and the MeCN molecules vary significantly. The longest Ag(3)−N(11) bond of 2.49(1) Å is 0.22 Å longer than that of the shortest Ag(9)−N(16) bond. This implies that some MeCN molecules may coordinate weakly at silver centres and some may bind tightly to silver atoms. This fact is con-

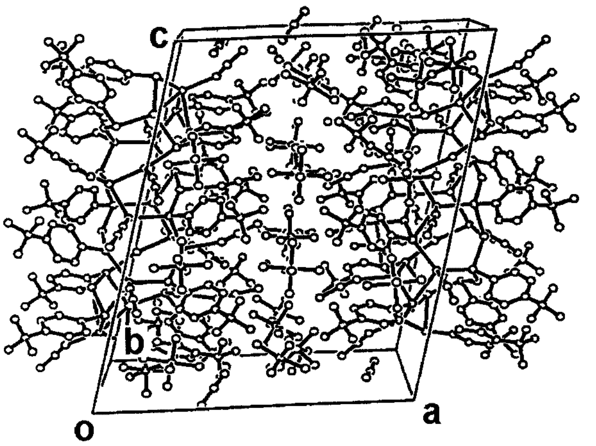


Figure 1. Cell packing diagram of **1** looking along the *b* axis; all hydrogen atoms have been omitted for clarity

sistent with two stages for the loss of MeCN molecules as indicated by the TGA curves. This is discussed later in the paper.

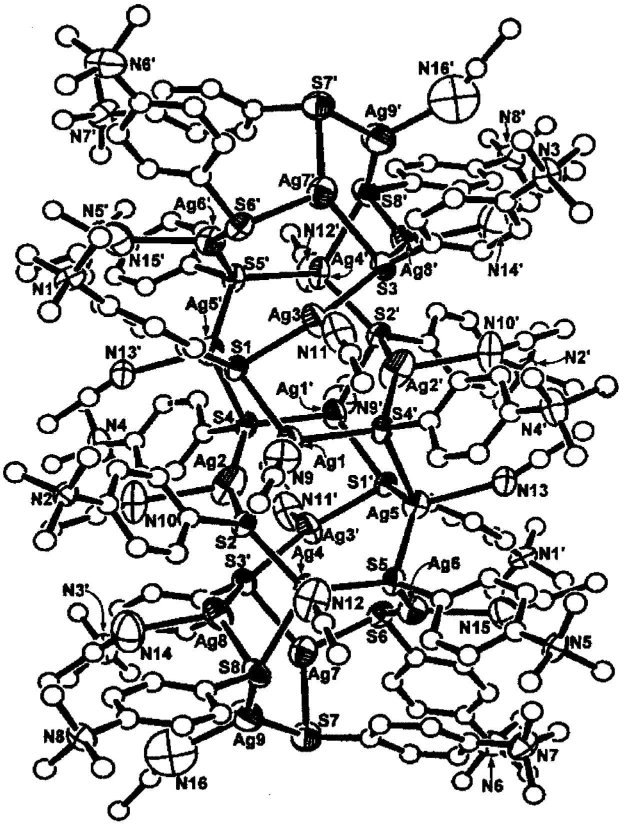


Figure 2. Perspective view of the $[Ag_9(Tab)_8(MeCN)_8]_2^{18+}$ ion of **1** including labelling scheme; thermal ellipsoids are shown at the 50% probability level; all hydrogen atoms have been omitted for clarity

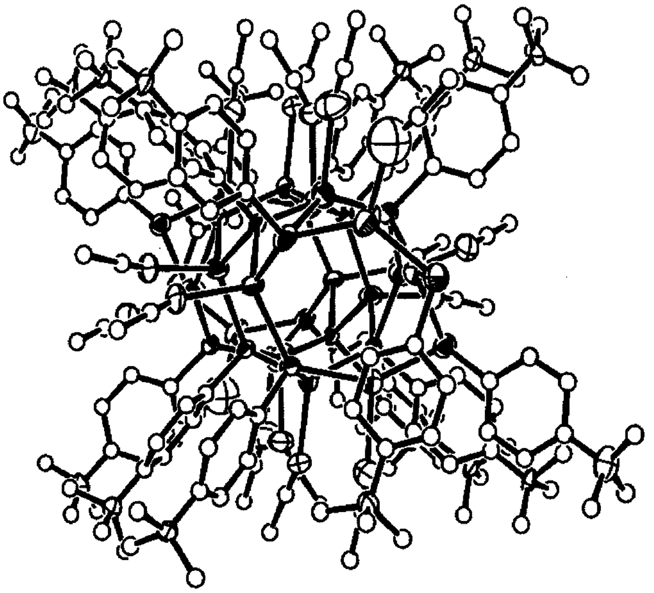


Figure 3. A side view of the tubular structure of the octadecacation of **1**, looking along the *c* axis

Table 1. Selected bond lengths [Å] and angles [°] for **1**

Ag(1)···Ag(2)	3.410(2)	Ag(1)···Ag(3)	3.426(2)
Ag(4)···Ag(8)	3.130(2)	Ag(5)···Ag(6)	3.195(2)
Ag(6)···Ag(7)	3.306(2)	Ag(7)···Ag(8)	3.424(2)
Ag(7)···Ag(9)	3.063(2)	Ag(8)···Ag(9)	3.011(3)
Ag(1)−S(1)	2.589(4)	Ag(1)−S(2)	2.654(5)
Ag(1)−S(4′)	2.503(5)	Ag(2)−S(2)	2.421(5)
Ag(2)−S(4)	2.410(5)	Ag(3)−S(1)	2.460(5)
Ag(3)−S(3)	2.455(6)	Ag(4)−S(2)	2.542(4)
Ag(4)−S(5)	2.486(5)	Ag(4)−S(8)	2.627(6)
Ag(5)−S(5)	2.531(6)	Ag(5)−S(1′)	2.537(5)
Ag(5)−S(4′)	2.638(4)	Ag(6)−S(5)	2.454(5)
Ag(6)−S(6)	2.399(5)	Ag(7)−S(6)	2.550(5)
Ag(7)−S(6)	2.553(6)	Ag(7)−S(7)	2.481(6)
Ag(7)−S(3′)	2.554(4)	Ag(8)−S(8)	2.530(5)
Ag(8)−S(3′)	2.526(5)	Ag(9)−S(7)	2.425(6)
Ag(9)−S(8)	2.455(6)	Ag(1)−N(9)	2.31(2)
Ag(2)−N(10)	2.49(2)	Ag(3)−N(11)	2.43(2)
Ag(4)−N(12)	2.35(2)	Ag(5)−N(13)	2.40(2)
Ag(6)−N(15)	2.44(2)	Ag(8)−N(14)	2.40(2)
Ag(9)−N(16)	2.27(4)		
S(1)−Ag(1)−S(2)	113.2(2)	S(1)−Ag(1)−N(9)	113.8(4)
S(2)−Ag(1)−N(9)	92.2(5)	S(4′)−Ag(1)−N(10)	116.0(4)
S(4′)−Ag(1)−S(1)	105.78(12)	S(2)−Ag(1)− S(4′)	116.2(1)
S(2)−Ag(2)−S(4)	151.6(2)	S(2)−Ag(2)−N(10)	94.9(5)
S(4)−Ag(2)−N(10)	108.5(5)	S(1)−Ag(3)−S(3)	143.5(2)
S(1)−Ag(3)−N(11)	108.8(6)	S(3)−Ag(3)−N(11)	107.7(6)
S(2)−Ag(4)−S(5)	111.2(2)	S(2)−Ag(4)−S(8)	107.3(2)
S(2)−Ag(4)−N(12)	114.5(5)	S(5)−Ag(4)−S(8)	115.9(2)
S(5)−Ag(4)−N(12)	111.3(5)	S(8)−Ag(4)−N(12)	96.0(6)
S(1′)−Ag(5)−N(13)	107.3(4)	S(4′)−Ag(5)−N(13)	93.7(4)
S(1′)−Ag(5)−S(4′)	99.28(5)	S(1′)−Ag(5)−S(5)	125.26(12)
S(4′)−Ag(5)−S(5)	111.80(11)	S(5)−Ag(5)−N(13)	114.1(4)
S(5)−Ag(6)−S(6)	143.8(2)	S(5)−Ag(6)−N(15)	97.0(4)
S(6)−Ag(6)−N(15)	116.5(4)	S(6)−Ag(7)−S(7)	114.9(2)
S(3′)−Ag(7)−S(6)	100.61(12)	S(3′)−Ag(7)−S(7)	91.5(6)
S(3′)−Ag(8)−S(8)	136.05(13)	S(3′)−Ag(8)−N(14)	102.2(6)
S(8)−Ag(8)−N(14)	109.8(6)	S(7)−Ag(9)−S(8)	132.5(2)
S(7)−Ag(9)−N(16)	106.7(8)	S(8)−Ag(9)−N(16)	120.0(8)
Ag(1)−S(1)−Ag(3)	85.4(1)	Ag(5′)−S(1)−Ag(3)	110.0(2)
Ag(5′)−S(1)−Ag(1)	127.2(2)	Ag(1)−S(2)−Ag(2)	84.3(2)
Ag(1)−S(2)−Ag(4)	106.0(2)	Ag(2)−S(2)−Ag(4)	135.4(2)
Ag(8′)−S(3)−Ag(7′)	84.7(1)	Ag(7′)−S(3)−Ag(3)	94.1(2)
Ag(8′)−S(3)−Ag(3)	134.9(2)	Ag(5′)−S(4)−Ag(2)	101.4(2)
Ag(1′)−S(4)−Ag(2)	119.9(2)	Ag(5′)−S(4)−Ag(1′)	112.0(2)
Ag(4)−S(5)−Ag(5)	119.0(2)	Ag(4)−S(5)−Ag(6)	124.1(2)
Ag(6)−S(5)−Ag(5)	79.7(2)	Ag(6)−S(6)−Ag(7)	83.7(2)
Ag(7)−S(7)−Ag(9)	76.2(2)	Ag(8)−S(8)−Ag(4)	74.7(2)
Ag(8)−S(8)−Ag(9)	74.3(2)	Ag(4)−S(8)−Ag(9)	130.0(2)

Interestingly, when crystals of **1** were heated in vacuo at 150 °C for 1 h, a yellow solid **1b** was formed and the liberation of MeCN was apparent by collection in a cold trap. When **1b** was immersed in MeCN, colourless crystals of **1** (identified by X-ray crystallography) were formed again in almost quantitative yield. What are the identities of **1a** and **1b**? We made numerous attempts to grow crystals of **1a** and **1b** in other solvents such as acetone and DMSO but were unsuccessful. Elemental analyses of **1a** and **1b** are in agreement with the formula $[Ag_9(Tab)_8]_2(PF_6)_{18}$. The FT-IR spectra of **1a** and **1b** are almost identical and display two strong peaks for PF_6 at 856 and 559 cm^{-1} but no C=N vibration at around 2262 cm^{-1} for **1**. The ^1H NMR spectra of both **1a** and **1b** in [D$_6$]DMSO exhibit only singlets at

δ = 3.34 ppm for the NMe_3 groups and multiplets in the δ = 7.43−7.48 ppm region for phenyl groups but no resonances for the methyl groups of MeCN molecules in the region of δ = 2.07 ppm. Not surprisingly, the UV/Vis spectra of **1**, **1a** and **1b** in MeCN exhibit the same strong and broad absorbance band at 284 nm (see Supporting Information, for Supporting Informations see also the footnote on the first page of this article) which may overlap the possible absorption bands in the visible region for **1**, **1a** and **1b**.

Crystals of **1** quickly lose some of the solvated MeCN molecules as soon as they are taken out of the mother liquor at room temperature. The surfaces of the crystals were observed to crack within seconds under the microscope. As shown in Figure 2, the thermogravimetric analysis revealed that **1** underwent decomposition in three stages between 25 and 400 °C. As shown in Figure 4, the first stage caused a weight loss of 4.5% in the region of 25−90 °C which corresponds roughly to the loss of three solvate MeCN molecules and another six coordinated MeCN molecules. The second stage resulted in a weight loss of 5.1% in the region of 90−160 °C, consistent with the loss of the remaining ten MeCN molecules in **1**. In the first stage, one more solvate MeCN molecule may be missing during the sample preparation for TGA measurement. However, **1a** and **1b** were relatively stable in the range of 25−160 °C. On heating further to 250 °C, samples of **1**, **1a** and **1b** began to decompose with almost the same pattern.

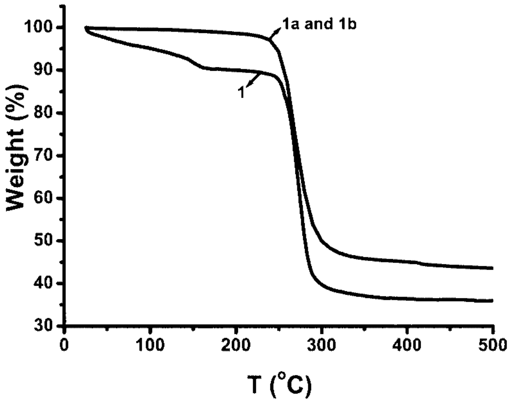


Figure 4. TGA curves for **1**, **1a** and **1b** under nitrogen

X-ray powder diffraction measurements for **1**, **1a** and **1b** gave data which was a little bit weak with a noisy baseline (see Supporting Information). However, the powder patterns of **1a** and **1b** resemble that of **1** which indicates that **1a** and **1b** may possess the $[Ag_{18}S_{16}]$ cluster core framework of **1**.

Compounds **1**, **1a** and **1b** exhibit luminescence in the solid state at ambient temperature. As shown in Figure 5, compound **1** exhibits an intense emission band at 625 nm (λ_{ex} = 450 and 507 nm) while **1a** and **1b** exhibit a similar emission band at 627 nm (λ_{ex} = 457 nm). As the free Tab ligand is not emissive in the solid state at ambient temperature, the possible origins of these emissions may be tentatively assumed to be MLCT from silver (4d) to the ligand (π^*) or an LC transition from S (nonbonding 3p) to the benzene ring (π^*) of the Tab ligands, though the metal-centred transition arising from the silver−silver contacts and transitions from surface S−Ar states cannot be ruled out.[2f,16]

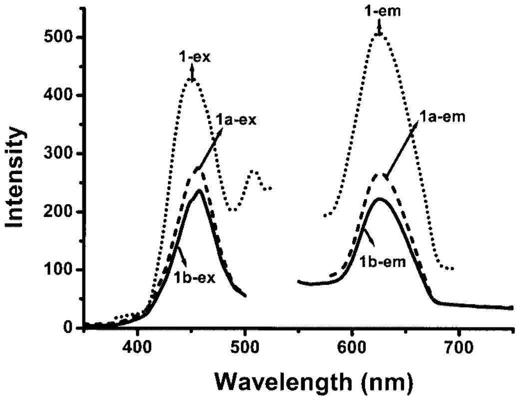


Figure 5. Excitation and emission spectra of **1**, **1a** and **1b** in the solid state at ambient temperature

Conclusions

In summary, we have successfully prepared a new silver thiolate complex from solid-state reactions between AgAc and $TabHPF_6$ at room temperature. When the solid-state product $[Ag_9(Tab)_8]_2(PF_6)_{18}$ was recrystallized from MeCN, it was solvated by MeCN molecules and some Ag atoms in its framework were coordinated by MeCN molecules, forming the unusual silver thiolate cluster **1**. The isolation of **1** provides convincing evidence that some solid-state products may have their structures altered, or at least experience changes in the coordination geometries of certain metal atoms in their structures when they are extracted with a solvent. The facile room-temperature solid-state synthesis reported in this paper is in accord with the current trend in green chemistry. Further investigation on the preparation of other metal/Tab complexes by this method is currently under way in our laboratory.

Experimental Section

General: $TabHPF_6$ was prepared according to a literature method.[12] Other chemicals and reagents were obtained from commercial sources and used as received. All solvents were pre-dried with activated molecular sieves and heated to reflux in the presence of appropriate drying agents under argon. IR spectra were recorded with a Nicolet MagNa-IR 550 instrument as KBr disk (4000−400 cm^{-1}). ^1H NMR spectra were recorded at ambient temperature with a Varian UNITYplus-400 spectrometer. ^1H NMR chemical shifts were referenced to the $[D_6]$DMSO signal. UV/Vis spectra were measured with a Hitachi U-2810 spectrophotometer. Elemental analyses for Ag and P were carried out by inductively coupled plasma atomic emission spectroscopy (Leeman PLA-SPECI ICP spectrophotometer). The elemental analyses for C, H and N were performed with an EA1110-CHNS elemental analyser. The thermal analysis was performed with a Perkin−Elmer TGA-7 thermogravimetric analyser at a heating rate of 10 °C/min and a flow rate of 100 cm^3/min (N_2). XRD spectra were recorded with a Rigaku D/MAX-IIIC X-ray diffractometer.

Preparation of $[Ag_9(Tab)_8(MeCN)_8]_2(PF_6)_{18}\cdot 4MeCN$ (1): A mixture of argenteous AgAc powder (0.33 g, 2 mmol) and white $TabHPF_6$ powder (0.63 g, 2 mmol) was placed in an open agate mortar and ground at room temperature for 0.5 h. During this time, the mixture gradually became yellow and a strong smell of acetic acid was apparent. The mixture was washed with CH_3OH/Et_2O (3:1) and dried in vacuo to form 0.78 g of a yellow solid (**1a**). $C_{144}H_{208}Ag_{18}F_{108}N_{16}S_{16}P_{18}$ (7227.2): calcd. C 23.93, H 2.90, Ag 26.87, N 3.10, P 7.71; found C 24.12, H 3.28, Ag, 26.23, N 3.55, P, 7.58. IR (KBr disc): $\tilde{\nu}$ = 1624 (w), 1489 (s), 1126 (s), 1010 (m), 856 (s), 744 (s), 559 (m) cm^{-1}. UV/Vis (MeCN): $\lambda_{max.}$ (ε [$M^{-1}\cdot cm^{-1}$]) = 282 (220000) nm. ^1H NMR (400 MHz, [D_6]DMSO): δ = 7.43−7.48 (m, 4 H, Ph), 3.34 (s, 9 H, NMe_3) ppm. Into a glass beaker containing **1a** (0.78 g) was added MeCN (10 mL) immediately forming a yellow solution. Colourless crystals of $[Ag_9(Tab)_8(CH_3CN)_8]_2(PF_6)_{18}\cdot 4CH_3CN$ (**1**) were isolated by layering diethyl ether (10 mL) onto the solution for one week. The crystals were collected by filtration and washed with $MeOH/Et_2O$ (1:4) Yield: 0.85 g (95%). $C_{184}H_{268}Ag_{18}F_{108}N_{36}P_{18}S_{16}$ (8048.3): calcd. C 27.46, H 3.36, Ag 24.13, N 6.26, P 6.93; found C 27.89, H 3.28, Ag 23.85, N 6.65, P 6.73. IR (KBr disc): $\tilde{\nu}$ = 2262 (w), 1628 (w), 1489 (s), 1126 (w), 1010 (w), 841 (s), 744 (w), 559 (m) cm^{-1}. UV/Vis (MeCN): $\lambda_{max.}$ (ε [$M^{-1}\cdot cm^{-1}$]) = 283 (180000) nm. ^1H NMR (400 MHz, [D_6]DMSO): δ = 7.43−7.48 (m, 16 H, Ph), 3.34 (s, 36 H, NMe_3), 2.07 (s, 12 H, MeCN) ppm. Crystals of **1** suitable for X-ray analysis were obtained by recrystallization from MeCN.

De-solvation and Re-solvation Experiments: Colourless crystals of **1** (0.805 g, 0.1 mmol) were placed in a Pyrex glass tube which was connected to a cold trap. The tube was heated to 150 °C and allowed to stand at that temperature for 10 h. During this period, the colour of **1** gradually turned from white to yellow. After it was cooled to room temperature, 0.72 g of yellow solid **1b** had formed. To a glass beaker containing **1b** (0.3 g) was added MeCN (5 mL) forming a yellow solution. Similar workup generated colourless crystals of **1** (confirmed by X-ray crystallography) in 98% yield. **1b:** $C_{144}H_{208}Ag_{18}F_{108}N_{16}S_{16}P_{18}$ (7227.2): calcd. C 23.93, H 2.90, Ag 26.87, N 3.10, P 7.71; found C 23.62, H 2.56, Ag 26.45, N 3.42, P 7.60. IR (KBr disc): $\tilde{\nu}$ = 1620 (w), 1493 (s), 1126 (m), 1010 (m), 856 (s), 744 (s), 559 (m) cm^{-1}. UV/Vis (MeCN): $\lambda_{max.}$ (ε [$M^{-1}\cdot cm^{-1}$]) = 282 (240000) nm. ^1H NMR (400 MHz, [D_6]DMSO): δ = 7.43−7.48 (m, 4 H, Ph), 3.34 (s, 9 H, NMe_3) ppm.

X-ray Crystal Structure Determination of 1: All measurements were carried out with a Rigaku Mercury CCD X-ray diffractometer (3 kV, sealed tube) using graphite-monochromated Mo-K_α radiation (λ = 0.71070 Å). A colourless single-crystal of **1** with dimensions of 0.30 × 0.30 × 0.30 mm was mounted at the top of a glass fibre and cooled to 193 K in a stream of gaseous nitrogen. Diffraction data were collected in the ω mode with a detector-to-crystal distance of 35 mm. Indexing was performed from 6 images each of which resulted from a 15 s exposure. Cell parameters were refined using the program CrystalClear (Rigaku and MSc, Ver. 1.3, 2001) on all observed reflections with θ between 3.0° and 27.5°. A total of 720 oscillation images were collected in the range $1.96° < 2\theta < 54.9°$. The collected data were reduced 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 0.498 to 0.648. The data were also corrected for Lorentz and polarization effects. The structure of **1** was solved by direct methods[17] and refined by full-matrix least squares on F.[18] Non-hydrogen atoms except P(5) to P(10), F(1) to F(6), N(16) to N(18), C(7) to C(9), C(34) to C(36), C(52) to C(54) and C(87) to C(92) were refined anisotropically. The two PF_6^- anions bearing P(8) and P(10) were refined using restrained parameters as rigid groups with occupancy factors of 0.5. All hydrogen atoms were placed in calculated positions and refined in the final structure-factor refinement. There may be more than two free acetonitrile solvent molecules in the asymmetric unit. However, attempts to locate other acetonitrile molecules were unsuccessful. Besides, the relatively high thermal parameters of the F atoms of the PF_6^- anions of P(5) to P(10) and some carbon atoms [C(7) to C(9), C(34) to C(36), C(52) to C(54) and C(87) to C(92)] of the NMe_3 groups showed signs of disorder, but attempts to model these disorders did not succeed. The relatively high R values may be due to the quality of the crystal and the possible disorder of the methyl groups, part of the PF_6^- anions and part of the acetonitrile molecules. Neutral atom-scattering factors were taken from Cromer and Waber.[19] Anomalous dispersion effects were included in $F_{calcd.}$.[20] All calculations were performed with a Dell workstation using the CrystalStructure crystallographic software package. Crystal and data collection parameters for **1** are summarised in Table 2. CCDC-229000 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Summary of the crystal data for **1**

Empirical formula	$C_{184}H_{268}Ag_{18}F_{108}N_{36}P_{18}S_{16}$
Formula mass	8048.32
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	18.114(3)
b [Å]	18.311(3)
c [Å]	23.680(4)
α [°]	84.653(8)
β [°]	75.970(7)
γ [°]	89.252(9)
V [$Å^3$]	7586.3(21)
$D_{calcd.}$ [$g\cdot cm^{-3}$]	1.762
Z	1
μ [cm^{-1}]	14.48
Reflections [$I > 3.00\sigma(I)$]	12874
Parameters	1488
R[a]	0.0890
R_w[b]	0.0940
GOF[c]	1.144
Largest residual peak/hole [$e\cdot Å^{-3}$]	1.99/−1.14

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $Rw = \{w\Sigma(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$. [c] GOF = $\{\Sigma w(|F_o| - |F_c|)^2/(M - N)\}^{1/2}$, where M is the number of reflections and N is the number of parameters.

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