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Trimethylphosphite stabilized disilver(I) methanedisulfonates as MOCVD precursors

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ABSTRACT

New disilver(I) methanedisulfonates complexes $\{CH_2(SO_3)_2Ag_2: [P(OMe)_3]_n\}$ (n = 2, 2a; n = 4, 2b; n = 6, 2c) were prepared by reacting $[CH_2(SO_3)_2Ag_2]$, which could be synthesized from methanedisulfonic acid and Ag_2CO_3 in water, with trimethylphosphite in dichloromethane. The molecular structure of 2a was determined using X-ray single crystal analysis. Complex 2a exhibits an infinite chain structure with eightmembered rings (AgOSOAgOSO) fully interconnected by the third sulfonic O atoms. Complex 2b was used to deposit silver films by metal organic chemical vapor deposition (MOCVD) for the first time. The silver film obtained was characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersion X-ray analysis (EDX).

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1. Introduction

In recent years, silver has received considerable attention in many fields of materials science due to it having the lowest resistivity and highest thermal conductivity of all metals [1,2]. For example, silver films have been reported as contacts in microelectronics [3], as a component of high-temperature superconducting materials [4], magnetics [5] or bactericidal coatings [6]. Silver films have been deposited by various methods, such as sputtering [7], thermal evaporation [8], electron-beam evaporation [9] and chemical vapor deposition (CVD) [10]. Among these techniques, metal organic chemical vapor deposition (MOCVD) is a very effective technique for the growth of silver with high quality because of its high deposition rates with good step coverage [11] and the high aspect ratio in the multilevel metallization structure [12].

One of the major problems in silver-MOCVD is the selection of appropriate silver(I) precursors. The silver precursors most often used are diverse inorganic and organometallic precursors, including AgF [8], $[(C_4F_7)Ag]_n$ [13], $(\beta$ -diketonato)Ag(PR₃) [14,15], (hfa-c)Ag(CNMe) [16] various organophosphine stabilized silver carboxylates [17], silver methanesulfonates [18,19] and silver succinimide [20]. The majority of the silver salts and complexes are completely involatile [21], although this can be overcome when tertiary phosphines are used as secondary ligands. Organometallic silver compounds with tertiary phosphines are used in the CVD of silver layers, for example, $[(hfac)Ag(PMe_3)_n]$ with no carrier gas, deposition temperature 523–623 K, system pressure 6.7 Pa [22];

[(fod)Ag(PMe₃)] with the carrier gas H₂, deposition temperature 503–573 K, system pressure 13.3 Pa [23]; [(CF₃COO)Ag(PⁿBu₃)] with the carrier gas Ar, deposition temperature 480–590 K, system pressure 101.3 Pa [24]. Thus, new classes of silver(I) precursors are highly desirable. Known for their good chelating ability, the class of cyclic β-diketones can impart desired chemical and physical properties as well as modulating the volatility. Silver methanedisulfonate exhibits a novel structure with six-membered rings like cyclic β-diketones and there are only a few reports about its metal complexes [25]. In this paper, we reported the synthesis of trimethylphosphite stabilized silver(I) methanedisulfonates which were used as precursors for the deposition of silver by using MOC-VD techniques for the first time. The single crystal structure of **2a** has been determined and is discussed as well.

2. Experimental

2.1. General procedures

All operations were carried out under an atmosphere of purified nitrogen with standard Schlenk techniques. The solvent dichloromethane (CH₂Cl₂) was purified by distillation from P₂O₅ under N₂ before use. ¹H NMR were recorded on a Bruker Advance 300 spectrometer operating at 300.130 MHz in the Fourier transform mode; ¹³C{¹H} NMR spectra were recorded at 75.467 MHz. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane (δ = 0.0 ppm) with the solvent as the reference signal (¹H NMR, D₂O δ = 4.79, CDCl₃ δ = 7.26; ¹³C{H} NMR, CDCl₃ δ = 77.55). Infrared spectra were collected on a Bruker Vector 22 in KBr at room temperature. Elemental analyses were performed





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on a Perkin-Elmer 240 C elemental analyzer. Thermogravimetric studies (TG) and differential scanning calorimetric (DSC) studies were carried out with a NETZSCH STA 409 PC/PG with a constant heating rate of 10 $^\circ C\ min^{-1}$ under N_2 (30 $cm^3\ min^{-1})$. Melting points were observed in sealed capillaries and are uncorrected. The MOCVD experiments were carried out in a vertical quartz tube hot-wall MOCVD reactor, 60 mm in diameter. Heating was achieved by a resistively heated tube oven (AICHUANG Company). The temperature was set by the temperature control FP 93 (SHI-MADEN Company) and was calibrated with a thermocouple type SR 3 (SHIMADEN Company) digital thermometer. The precursor container was heated with a heating band for evaporation of the precursor. The precursor vapor was transported to the reactor tube by N₂ carrier gas. The carrier gas flow was regulated using a D07-7B (SEVENSTAR Company) mass flow controller which was connected to the apparatus by a section of flexible stainless steel tubing. The pressure control system consisted of a cooling trap and a FT-110 (KYKY Company) molecular pump unit. The trap prevents the reactor effluents from entering the vacuum pump. The film thickness was measured with an Ambios Technology XP-1 Profilometer. The powder X-ray diffraction pattern was recorded on a D8 ADVANCE X-ray diffractometer. SEM images and EDX analysis were carried out with an Hitachi Model S-4800 with scanning electron microscope and an energy dispersive X-ray detector.

2.2. Synthesis

2.2.1. Synthesis of $[CH_2(SO_3)_2Ag_2]$ (1)

Methanedisulfonic acid (4.58 g, 0.026 mol) dissolved in 30 mL of H₂O was added dropwise into a stirred suspended solution of [Ag₂CO₃] (7.72 g, 0.028 mol) in 20 mL of H₂O at 20 °C. A clear solution was obtained by filtration through a pad of Celite after stirring the reaction mixture for 1 h at 20 °C. A white solid product was obtained after removing water in a rotary evaporator and drying in a vacuum oven at 50 °C. The product was stored under nitrogen and kept in a dark place. Yield: 8.52 g (84%, based on Ag₂CO₃). It could be also synthesized by reacting methanedisulfonic acid with Ag₂O in water [26]. M.p.: 306 °C dec. ¹H NMR (D₂O) δ: 4.4 (s. 2 H, CH₂-H). IR (KBr) data (cm⁻¹): 3029 (w), 2978 (w), 1271 (m), 1229 (vs), 1080 (w), 1023 (s), 814 (m), 772 (w), 589 (m), 537 (w), 516 (m).

2.2.2. Synthesis of $\{CH_2(SO_3)_2Ag_2, [P(OMe)_3]_2\}$ (**2a**)

Trimethylphosphite (0.3723 g, 3.00 mmol) dissolved in 20 mL of CH₂Cl₂ was added dropwise into a stirred solution of [CH₂(SO₃)₂Ag₂] (0.5848 g, 1.50 mmol) suspended in 20 mL of CH₂Cl₂ at 0 °C. A clear solution was obtained by filtration through a pad of Celite after stirring the reaction mixture for 6 h at 0 °C. A white solid was obtained after removing all the volatiles in oilpump vacuo, Yield: 0.90 g (94%, based on [CH₂(SO₃)₂Ag₂]. M.p.: 69 °C dec. Anal. Calc. for C₇H₂₀O₁₂Ag₂P₂S₂: C, 13.18; H, 3.16. Found: C, 13.13; H, 3.05%. ¹H NMR (CDCl₃) δ: 4.5 (s, 2 H, CH₂–H), 3.7 (d, 18 H, J_{PH} = 13.7 Hz, CH₃-H). ¹³C{¹H} NMR (CDCl₃) δ : 68.1 (CH₂), 51.8 $(I_{PC} = 5.2 \text{ Hz}, \text{ CH}_3)$. IR (KBr) data (cm⁻¹): 3029 (m), 2975 (m), 2839 (m), 1461 (m), 1381 (m), 1273 (s), 1223 (vs), 1077 (m), 1022 (vs), 812 (s), 761 (s), 636 (m), 589 (s), 535 (m), 517 (s).

2.2.3. Synthesis of $\{CH_2(SO_3)_2Ag_2 \cdot [P(OMe)_3]_4\}$ (**2b**)

Complex **2b** was synthesized by following the same procedure, only using $[CH_2(SO_3)_2Ag_2]$ (0.5848 g, 1.50 mmol) and trimethylphosphite (0.7446 g, 6.00 mmol). After appropriate work-up, complex 2b was obtained as a colorless liquid. Yield: 1.21 g (91 %, based on [CH₂(SO₃)₂Ag₂]). Anal. Calc. for C₁₃H₃₈O₁₈Ag₂P₄S₂: C, 17.62; H, 4.32. Found: C, 17.57; H, 4.24%. ¹H NMR (CDCl₃) δ: 4.4 (s, 2 H, CH₂-H), 3.7 (d, 36 H, J_{PH} = 12.9 Hz, CH₃-H). ¹³C{¹H} NMR $(CDCl_3)$ δ : 68.5 (CH_2) , 51.5 $(I_{PC} = 4.4 \text{ Hz}, CH_3)$. IR (KBr) data (cm⁻¹): 2999 (m), 2953 (s), 2845 (m), 1461 (s), 1386 (m), 1253

(s), 1203 (s), 1073 (m), 1007 (vs), 788 (vs), 754 (vs), 634 (m), 579 (s), 521 (vs), 461 (m).

2.2.4. Synthesis of $\{CH_2(SO_3)_2Ag_2, [P(OMe)_3]_6\}$ (2c)

Complex **2c** was synthesized by following the same procedure, only using [CH₂(SO₃)₂Ag₂] (0.3899, 1.00 mmol) with trimethylphosphite (0.7446 g, 6.00 mmol). After appropriate work-up, complex **2c** was obtained as a colorless liquid. Yield: 1.04 g (92%, based on $[CH_2(SO_3)_2Ag_2]$). Anal. Calc. for $C_{19}H_{56}O_{24}Ag_2P_6S_2$: C, 20.12; H, 4.98. Found: C, 20.07; H, 4.89%. ¹H NMR (CDCl₃) δ: 4.3 (s, 2H, CH₂-H), 3.7 (d, 54 H, I_{PH} = 12.4 Hz, CH₃-H). ¹³C{¹H} NMR $(CDCl_3)$ δ : 68.4 (CH_2) , 50.9 $(I_{PC} = 3.6 \text{ Hz}, CH_3)$. IR (KBr) data (cm⁻¹): 2997 (m), 2953 (m), 2845 (m), 1460 (s), 1250 (s), 1202 (vs), 1069 (m), 1005 (vs), 788 (vs), 633 (m), 580 (vs), 520 (s), 459 (m), 414 (m).

2.3. X-ray structure determination

Single crystals of **2a** could be obtained by cooling a saturated dichloromethane solution to 253 K. A suitable crystal for X-ray determination was placed in glue under N₂ due to its sensitivity to oxygen and moisture. X-ray structure measurement was performed on a BRUKER SMART Apex CCD detector equipped with graphite monochromatic Mo K α radiation (λ = 0.71073 Å) at 153 K. Date collection and processing (cell refinement, data reduction and empirical absorption correction) were performed using the CRYSTALCLEAR program package [27]. The structure was solved using direct methods and refined by full-matrix least-squares procedures on F^2 (SHELX-97) [28]. All of the non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic data and details on refinement are presented in Table 1.

2.4. Metal organic chemical vapor deposition of 2b

The deposition of silver was conducted using a vertical quartz tube hot-wall MOCVD reactor with 2b as the precursor. As sub-

Table 1

Crystallographic data and analysis parameters for {CH₂(SO₃)₂Ag₂·[P(OMe)₃]₂}.

-		
	Formula	$C_7 H_{20} Ag_2 O_{12} P_2 S_2$
	Formula weight	638.03
	Space group	P2(1)/c
	Crystal size (mm)	0.2 imes 0.2 imes 0.2
	Crystal system	monoclinic
	Z value	4
	a (Å)	9.305(2)
	b (Å)	10.178(2)
	c (Å)	20.719(4)
	α (°)	90
	β(°)	98.52(3)
	γ (°)	90
	D_{calc} (g/cm ³)	2.184
	Index ranges	$-11 \leqslant h \leqslant 9$, $-11 \leqslant k \leqslant 12$,
		$-24 \leqslant l \leqslant 20$
	Crystal shape/color	prism/colorless
	F (0 0 0)	1256
	μ (Mo K $lpha$) (mm $^{-1}$)	2.45
	λ (Mo Kα) (Å)	0.71073
	Temperature (K)	153(2)
	θ range (°)	3.0-28.8
	Independent reflections	2653
	$[(I) > 2\sigma(I)]$	
	$R_1 \left[I > 2\sigma(\theta) \right]^a$	0.036
	$wR_2 [I > 2\sigma(\theta)]^b$	0.082
	Goodness-of-fit (GOF) on F ^{2c}	1.01
	$\Delta \rho_{\rm max} ({ m e}{ m \AA}^{-3})$	0.86
	$\Delta ho_{ m min}$ (e Å ⁻³)	-0.71

^a $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(wF_o^4)]^{1/2}$.

^b $w = 1/[\sigma^2(F_0^2) + (0.0483P)^2], P = (F_0^2 + 2F_0^2)/3.$ ^c $S = [\Sigma w(F_0^2 - F_0^2)^2]/(n - p)^{1/2}, n =$ number of reflections, p = parameters used.



 Table 2

 Selected bond lengths (Å) and bond angles (°) for {CH₂(SO₃)₂Ag₂·[P(OMe)₃]₂}.

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Bond lengths (Å)			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ag1-O8A	2.317(3)	Ag1–P1	2.329(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ag1-04	2.363(3)	Ag1-O6A	2.428(3)
$\begin{array}{ccccc} Ag2-09 & 2.371(3) & Ag2-07B & 2.510(3) \\ C7-S1 & 1.783(4) & C7-S2 & 1.790(4) \\ 04-S1 & 1.452(3) & 05-S1 & 1.454(3) \\ 06-S1 & 1.446(3) & 07-S2 & 1.447(3) \\ 08-S2 & 1.450(3) & 09-S2 & 1.450(3) \\ \hline Bond angles (^{\circ}) & & & \\ 08A-Ag1-P1 & 132.5(9) & 08A-Ag1-04 & 87.4(1) \\ P1-Ag1-04 & 129.9(9) & 08A-Ag1-06A & 84.1(1) \\ P1-Ag1-06A & 120.6 (8) & 04-Ag1-06A & 86.9(1) \\ 05-Ag2-P2 & 140.8(9) & 05-Ag2-09 & 80.3(1) \\ P2-Ag2-09 & 131.2(8) & 05-Ag2-07B & 86.0(1) \\ S1-04-Ag1 & 139.1(2) & S2-07-Ag2B & 143.1(2) \\ S1-C7-S2 & 116.6(2) \\ \hline \end{array}$	Ag2-05	2.306(3)	Ag2–P2	2.308(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ag2-09	2.371(3)	Ag2–O7B	2.510(3)
$\begin{array}{ccccccc} 04{-}\mathrm{S1} & 1.452(3) & 05{-}\mathrm{S1} & 1.454(3) \\ 06{-}\mathrm{S1} & 1.446(3) & 07{-}\mathrm{S2} & 1.447(3) \\ 08{-}\mathrm{S2} & 1.450(3) & 09{-}\mathrm{S2} & 1.450(3) \\ \hline Bond angles (^{\circ}) & & & \\ 08A{-}Ag1{-}P1 & 132.5(9) & 08A{-}Ag1{-}04 & 87.4(1) \\ P1{-}Ag1{-}04 & 129.9(9) & 08A{-}Ag1{-}06A & 84.1(1) \\ P1{-}Ag1{-}06A & 120.6 (8) & 04{-}Ag1{-}06A & 86.9(1) \\ 05{-}Ag2{-}P2 & 140.8(9) & 05{-}Ag2{-}09 & 80.3(1) \\ P2{-}Ag2{-}09 & 131.2(8) & 05{-}Ag2{-}07B & 88.7(1) \\ P2{-}Ag2{-}07B & 112.9(9) & 09{-}Ag2{-}07B & 86.0(1) \\ S1{-}04{-}Ag1 & 139.1(2) & S2{-}07{-}Ag2B & 143.1(2) \\ S1{-}C7{-}S2 & 116.6(2) \\ \hline \end{array}$	C7-S1	1.783(4)	C7-S2	1.790(4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	04-S1	1.452(3)	05-S1	1.454(3)
O8-S2 1.450(3) O9-S2 1.450(3) Bond angles (°) 08A-Ag1-O4 87.4(1) P1-Ag1-O4 129.9(9) 08A-Ag1-O6A 84.1(1) P1-Ag1-O6A 120.6 (8) 04-Ag1-O6A 86.9(1) O5-Ag2-P2 140.8(9) 05-Ag2-O9 80.3(1) P2-Ag2-O9 131.2(8) 05-Ag2-O7B 88.7(1) S1-04-Ag1 139.1(2) S2-07-Ag2B 143.1(2) S1-C7-S2 116.6(2)	06-S1	1.446(3)	07-S2	1.447(3)
Bond angles (°) O8A-Ag1-P1 132.5(9) O8A-Ag1-O4 87.4(1) P1-Ag1-O4 129.9(9) O8A-Ag1-O6A 84.1(1) P1-Ag1-O6A 120.6 (8) O4-Ag1-O6A 86.9(1) O5-Ag2-P2 140.8(9) O5-Ag2-O9 80.3(1) P2-Ag2-O9 131.2(8) O5-Ag2-O7B 88.7(1) P2-Ag2-O7B 120.9(9) O9-Ag2-O7B 86.0(1) S1-O4-Ag1 139.1(2) S2-O7-Ag2B 143.1(2) S1-C7-S2 116.6(2) S1-S1 S1-S1	08-S2	1.450(3)	O9-S2	1.450(3)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Bond angles (°)			
$\begin{array}{ccccc} P1-Ag1-O4 & 129.9(9) & 08A-Ag1-O6A & 84.1(1) \\ P1-Ag1-O6A & 120.6 (8) & 04-Ag1-O6A & 86.9(1) \\ 05-Ag2-P2 & 140.8(9) & 05-Ag2-O9 & 80.3(1) \\ P2-Ag2-O9 & 131.2(8) & 05-Ag2-O7B & 88.7(1) \\ P2-Ag2-O7B & 112.9(9) & 09-Ag2-O7B & 86.0(1) \\ S1-O4-Ag1 & 139.1(2) & S2-O7-Ag2B & 143.1(2) \\ S1-C7-S2 & 116.6(2) \end{array}$	08A-Ag1-P1	132.5(9)	08A-Ag1-04	87.4(1)
P1-Ag1-06A 120.6 (8) 04-Ag1-06A 86.9(1) 05-Ag2-P2 140.8(9) 05-Ag2-09 80.3(1) P2-Ag2-09 131.2(8) 05-Ag2-07B 88.7(1) P2-Ag2-07B 112.9(9) 09-Ag2-07B 86.0(1) S1-04-Ag1 139.1(2) S2-07-Ag2B 143.1(2) S1-C7-S2 116.6(2) 56-000 56-000	P1-Ag1-O4	129.9(9)	08A-Ag1-06A	84.1(1)
05-Ag2-P2 140.8(9) 05-Ag2-09 80.3(1) P2-Ag2-09 131.2(8) 05-Ag2-07B 88.7(1) P2-Ag2-07B 112.9(9) 09-Ag2-07B 86.0(1) S1-04-Ag1 139.1(2) S2-07-Ag2B 143.1(2) S1-C7-S2 116.6(2) 56-07-06 56-07-06	P1-Ag1-O6A	120.6 (8)	04-Ag1-06A	86.9(1)
P2-Ag2-09 131.2(8) 05-Ag2-07B 88.7(1) P2-Ag2-07B 112.9(9) 09-Ag2-07B 86.0(1) S1-04-Ag1 139.1(2) S2-07-Ag2B 143.1(2) S1-C7-S2 116.6(2) 143.1(2) 143.1(2)	05-Ag2-P2	140.8(9)	05-Ag2-09	80.3(1)
P2-Ag2-07B 112.9(9) 09-Ag2-07B 86.0(1) S1-04-Ag1 139.1(2) S2-07-Ag2B 143.1(2) S1-C7-S2 116.6(2) 143.1(2)	P2-Ag2-O9	131.2(8)	05-Ag2-07B	88.7(1)
S1-04-Ag1 139.1(2) S2-07-Ag2B 143.1(2) S1-C7-S2 116.6(2) 143.1(2)	P2-Ag2-O7B	112.9(9)	09-Ag2-07B	86.0(1)
S1-C7-S2 116.6(2)	S1-04-Ag1	139.1(2)	S2-07-Ag2B	143.1(2)
	S1-C7-S2	116.6(2)		

Scheme 1. Synthesis of complexes 2a-2c.

Symmetry code for A: -x, -1 + y, -z; B: -x + 1, -y + 1, -z.

strate pieces of silicon were applied, the typical deposition time was limited to 60 min. The precursor vessel temperature was maintained at 348 K by a heating band, with a nitrogen flow at 20 sccm to pick up the precursor vapor and transport into the reaction zone. The substrate susceptor was heated at 693 K by a resistive heating element. The total pressure was maintained at 70 Pa and the reaction by-products were exhausted by a pumping system. The deposition of Ag films was carried out in a reaction chamber (a hot-wall vertical cylindrical reactor). No reducing agent such as H₂ was used in the deposition processes. The average film thickness was about 0.7 μ m, giving a growth rate of 0.7 μ m h⁻¹.

3. Results and discussion

3.1. Synthesis

Metal organic silver precursors of the type $\{CH_2(SO_3)_2Ag_2 \cdot [P(O-Me)_3]_n\}$ (n = 2, **2a**; n = 4, **2b**; n = 6, **2c**) were prepared and used for this work. Compound $[CH_2(SO_3)_2Ag_2]$ (**1**) was synthesized by the reaction of methanedisulfonic acid with Ag_2CO_3 in water. The com-

plexes were synthesized by the interaction of $[CH_2(SO_3)_2Ag_2]$ (1) with $P(OMe)_3$ in stoichiometric ratios in CH_2Cl_2 , as shown in Scheme 1. The complexes were isolated in high yield (91–94%) as a white solid (2a) or colorless liquids (2b, 2c), which were stable under inert atmosphere for months at room temperature. On exposure to air they all decomposed in days to form brown products. Complexes 2a–2c were characterized by elemental analysis, FT-IR, ¹H and ¹³C{¹H} NMR spectroscopy (see Section 2).

As we know, the typical group vibration of sulfonates is in the range 1350–1050 cm⁻¹ [29,30]. In the IR spectra of **2a–2c**, the SO₃ groups show their characteristic group frequencies. The prominent absorptions in the ranges 1250–1270 and 1202–1223 cm⁻¹ can be attributed to the asymmetric and symmetric stretching vibration of SO₂ [31–35]. The absorptions around 1070 cm⁻¹ can be assigned as the stretching vibration of S–O, which is similar to a previous report [36]. Compared with the free trimethylphosphite (1012 cm⁻¹), the absorption bands of trimethylphosphite derived from P–O–C linkage stretching vibrations are shifted to lower frequencies for **2b–2c** by 5–7 cm⁻¹, but are shifted to higher frequencies for complex **2a** (1022 cm⁻¹) [37]. This may be caused by structural changes, but the real reason is unclear.



Fig. 1. A centrosymmetric tetranuclear fragment in the crystal structure of **2a**. The hydrogen atoms are omitted for clarity. Symmetry code for A: -x, -1 + y, -z; B: -x + 1, -y + 1, -z.



Fig. 2. The polymeric chain of complex 2a: (a) view along the b axis; (b) view along the c axis with methoxy groups omitted for clarity.



Fig. 3. TG curves of 2a-2c (heating rate 10 °C min⁻¹, nitrogen atmosphere).



Fig. 4. DSC curves of 2a-2c (heating rate 10 °C min⁻¹, nitrogen atmosphere).



Fig. 5. XRD pattern of the metallic silver thin film obtained from the MOCVD at 693 K using **2b** as precursor on a Si wafer.

The NMR spectra (¹H and ¹³C(¹H)) were recorded for all complexes at room temperature. In the ¹H NMR spectra, the integration area ratios are consistent with the stoichiometries of the complexes. The protons of complexes **2a–2c** in the methyl proton region appeared at 3.7 ppm. The proton of $-CH_2$ - in $-O_3SCH_2SO_3$ - appeared in the range 4.3–4.5 ppm as a single signal, which agrees well with a previous report [38]. In the ¹³C(¹H) NMR spectra of **2a–2c**, the carbon resonances of $-CH_2$ - on $-O_3SCH_2SO_3$ - show in a lower field region (68.1–68.5 ppm) compared to that of [P(OMe)₃] (50.9–51.8 ppm).

3.2. Single crystal structure of 2a

A single crystal of complex **2a** could be grown by slowly cooling a saturated dichloromethane solution containing **2a** to 253 K. The X-ray single crystal analysis results indicate that the molecular formula of complex **2a** is $\{CH_2(SO_3)_2Ag_2\cdot[P(OMe)_3]_2\}$. The centrosymmetric tetranuclear fragment in the crystal structure of **2a** is depicted in Fig. 1. Selected bond distances (Å) and bond angles (°) are given in Table 2.

Complex **2a** crystallizes in the monoclinic space group P2(1)/c, and is composed of centrosymmetric tetranuclear fragments (Fig. 1). A polymeric chain is formed (Fig. 2(a)), and it extends along the a axis and consists of { $CH_2(SO_3)_2Ag_2 \cdot [P(OMe)_3]_2$ }



Fig. 6. SEM image and EDX spectrum of the silver film obtained from the MOCVD at 693 K using 2b as precursor on a Si wafer.

fragments. Complex 2a represents a novel chain structure contained eight-membered rings (AgOSOAgOSO), which are connected by Ag atoms by the third sulfonic O atoms (Fig. 2(b)). The centrosymmetric tetranuclear fragment (Fig. 1) possesses a crystallographically imposed inversion symmetry with the inversion center in the centroid of the Ag_2O_2 core. The Ag(I) ion possesses a pseudo-tetrahedral environment set up by one P atom from the P(OMe)₃ ligand and three O atoms from different methanedisulfonate groups, with bond angles ranging from 80.2(2) to $140.8(2)^{\circ}$. The S–C–S angle $[116.6(2)^{\circ}]$ is larger than those of the reported complex [CH₂(SO₃)₂Ag₂] [111.8(4)°] [26], but close to another related complex with no ring in it, $[CH_2(SO_3)_2Ag_2]$ [116.4(7)°] [26]. The Ag1–O4 [2.363(3) Å] distance of the Ag_2O_2 core is shorter than another connective bond, Ag2-O7B [2.510(3) Å], similar to the situation in complex {[CH₂(SO₃)₂Ag₂·[P(OEt)₃]₂}₄ (connective bonds Ag–O: 2.355(2), 2.593(2) and 2.526(2)Å) [39]. In addition, the Ag–P distances in complex **2a** [2.329(2) and 2.308(2) Å] are shorter than the sum of the covalent radii of the P and Ag atoms (2.44 Å) [40] and that of complex $[(R_3P)_2AgPI]$ (PI = $C_8H_4NO_2$) [2.494(7)Å] [41].

3.3. Thermal analysis

Themogravimetry (TG) and differential scanning calorimetry (DSC) studies are required to optimize the temperature at which the respective single silver precursor should be maintained during the CVD experiments. The TG and DSC curves of complexes **2a–2c** are shown in Figs. 3 and 4. The decomposition of all the complexes is completed at ca. 400 °C. It can be seen from the DSC curves that complexes **2a** and **2c** possess at least two exothermic and/or endo-thermic steps, but for complex **2b** only one apparent endothermic process exists, from 94 to 450 °C with peak temperatures at 219 and 325 °C. It can be seen that the metal–organic **2a** starts to decompose (ca. 120 °C) at a much higher temperature than both **2b** and **2c** (ca. 90 °C), which most probably can be explained by the higher aggregation of **2a**.

For complex **2b**, it may lose two $P(OMe)_3$ groups from 94 to 185 °C with a corresponding weight loss of about 27.93%, which is approximately equal to the theoretical loss (28.00%). Then, it may lose other two $P(OMe)_3$ groups from 185 to 234 °C with a corresponding weight loss of about 27.54% which is again close to the theoretical loss (28.00%). It is very difficult to know the real thermal decomposition mechanism of methanedisulfonates. The final percentage of the residue is 24.40%, which is approximately equal to the theoretical value of silver (24.34%). However, the final percentages of the residues for **2a** and **2c** are 37.89 and 29.57%, respectively, which are little bit higher than the theoretical value of silver (33.81% and 19.02%), indicating there may be some impurities or the incomplete decomposition of the complexes.

In general, a liquid precursor is better than a solid precursor owing to its constant vapor pressure. The disilver complexes decompose with the release of the auxiliary ligands first, and some impurities or incomplete decomposition for the complexes **2a** and **2c**. In addition, the thermal measurement shows that complex **2b** should be suitable as a MOCVD precursor, and it has more a suitable thermal decomposition and thermal stability compared with that of {[(MeO)₃P]₂·AgO₃SCH₃} [19]. This may be due to its novel structure with six-membered rings, like cyclic β -diketonates, giving good chelating ability to the disilver(I) methanedisulfonates complexes. Considering the thermal properties obtained from the TG and DSC studies, we chose **2b** as a precursor for the CVD experiment.

3.4. Silver film studies

The surface morphology and composition of the silver films from the MOCVD experiment using **2b** were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersion X-ray analysis (EDX). The layer deposited is silver colored. The structure of the films was established by XRD. Irrespective of the reaction atmosphere, the XRD investigation showed the characteristic peaks of polycrystalline cubic metallic silver corresponding to the Ag(1 1 1), Ag(2 0 0), Ag(2 2 0), Ag(3 1 1) and Ag(2 2 2) reflections, as reported by JCPDS data (Fig. 5), with no preferential orientation of the growth.

SEM (Fig. 6) studies show that the film is composed of many well isolated, granular particulates spreading all over the substrate surface. The sizes of the silver grains are in the range 60–100 nm. The EDX spectrum (Fig. 6) of the deposited film shows Ag as the main component. Because of the discontinuous Ag particles exposing the substrate and the relatively high penetration depth of the electron beam during the EDX analysis, silicon as a substrate component was detected. Other light elements, such as C, O and P, which might be present as impurities or formed by surface oxidation of silver, are below the detection limit.

4. Conclusions

A straightforward synthesis methodology for the preparation of new disilver(I) methanedisulfonate complexes of the composition $\{CH_2(SO_3)_2Ag_2 \cdot [P(OMe)_3]_n\}$ (n = 2, n = 4, n = 6) is described. The molecular structure of **2a** exhibits a novel structure with six-membered rings like cyclic β -diketonates. On the basis of the properties of complexes **2a–2c**, we chose **2b** as a potential CVD precursor to grow silver films for the first time. The silver film is composed of many well isolated, granular particulates spreading all over the substrate surface. It has been demonstrated that the complex is a promising candidate as a precursor for the deposition of Ag.

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Appendix A. Supplementary data

CCDC 801254 contains the supplementary crystallographic data for compound 2a. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cam bridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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