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Anion-controlled Formation of Silver(I) Complexes of A Hexaazamacrocyclic Schiff Base: Synthesis, Structures and Electrochemistry

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Six silver(I) complexes of a macrocyclic Schiff Base (*L*) with different counter anions have been prepared and structurally characterized, where *L* is a hexaazamacrocyclic Schiff Base derived from the [2 + 2] condensation of terephthalaldehyde and 3-azapentane-1, 5-diamine. $[Ag_2L(NO_3)_2]$ (1) crystallizes in the triclinic space group $P\bar{1}$, with $a = 7.705(7)$, $b = 7.926(5)$, $c = 12.06(1)$ Å, $\alpha = 90.33(1)$, $\beta = 95.13(1)$, $\gamma = 104.07(1)^{\circ}$, $V = 711(1)$ Å^3 and $Z = 1$. $[Ag_2L(NO_3)_2]$ (2) crystallizes in the monoclinic $P2_1/n$, with $a = 7.714(3)$, $b = 14.491(7)$, $c = 11.821(6)$ Å, $\beta = 98.99(1)^{\circ}$, $V = 1305(1)$ Å^3 and $Z = 2$. $[Ag_3L_2(NO_3)_2](ClO_4)$ (3) crystallizes in the monoclinic space group $C2/m$, with $a = 14.950(6)$, $b = 13.258(3)$, $c = 27.399(16)$ Å, $\beta = 109.15(1)^{\circ}$, $V = 2589(2)$ Å^3; and $Z = 2$. $[Ag_2L_2](PF_6)_2$ (4) crystallizes in the monoclinic space group $P2_1/n$, with $a = 10.066(3)$, $b = 9.846(5)$, $c = 27.40(2)$ Å, $\beta = 92.81(8)^{\circ}$, $V = 1712(2)$ Å^3 and $Z = 4$. $[Ag_4L(MeCH(OH)CO_2)_4]$ (5) crystallizes in the monoclinic $P2_1/c$, with $a = 13.851(9)$, $b = 8.043(3)$, $c = 19.65(1)$ Å, $\beta = 107.73(2)^{\circ}$, $V = 2085(2)$ Å^3 and $Z = 2$. $[Ag_4L(PhCO_2)_4]_n \cdot nAg_2(PhCO_2)_2$(6) crystallizes in the triclinic $P\bar{1}$, with $a = 10.896(9)$, $b = 10.990(3)$, $c = 13.25(1)$ Å, $\alpha = 75.88(1)$, $\beta = 87.60(1)$, $\gamma = 82.91(1)^{\circ}$, $V = 1527(2)$ Å^3 and $Z = 3$. 1 and 2 are a pair of isomers crystallized in the triclinic and monoclinic forms with the nitrate groups acting in the bidentate chelate and monodentate modes, respectively. 3 has a discrete trinuclear $[Ag_3L_2(NO_3)_2]^+$ cation, in which the central metal atom is ligated by three nitrogen atoms from one *L* ligand and one amine nitrogen atom from the other *L* ligand, while at each side, the metal atom is coordinated by three nitrogen atoms from one *L* ligand and one nitrate oxygen atom. In 4, a pair of silver(I) atoms are wrapped by a pair of *L* ligands to form a dimeric cation with each metal atom being coordinated by three nitrogen atoms from one *L* ligand and one amine nitrogen atom from the other *L* ligand. 5 is a tetranuclear complex, a pair of metal atoms bridged by a μ_2-lactate group are ligated in a triaza site with one metal atom linked to two nitrogen atoms and the other metal atom to one nitrogen atom and one monodentate lactate group. The crystal structure of 6 comprises infinite one-dimensional $[Ag_4L(PhCO_2)_4]_n$ chains and the discrete dimeric $Ag_2(PhCO_2)_2$ species. Each *L* ligand binds two inversely-related silver(I) atoms, while each of the two metal atoms is bridged by a single μ_2-benzoate group to a bis(μ_2-benzoate) disilver(I) core, resulting in the polymeric chain. The discrete dimeric $Ag_2(PhCO_2)_2$ species are inserted into the cavities constructed by the polymeric chains in 6, and interact with the chains through metal-oxygen contacts and π–π stacking interaction. The redox properties of the six compounds have also been investigated by cyclic voltammetry.

Keywords: Silver(I) compounds, polyazamacrocycle schiff base, electrochemistry

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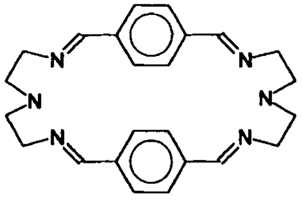
1. INTRODUCTION

During the past two decades there has been considerable interest in macrocyclic compounds, because the rich coordination chemistry can be utilized in biomimetics, catalysis and material science [1-3]. One of the interesting macrocycles is the dinucleating polyazamacrocyclic ligands, which have been found to be capable of simultaneous binding of metal ions in close proximity to provide models of biological dimetallic sites [4-7]. Although many polyazamacrocyclic complexes containing copper(II), zinc(II), cobalt(II, III) and nickel(II) have been described [4-7], only a very limited number of silver(I) complexes have been recently documented, most of which are dinuclear silver(I) complexes [8-10]. Moreover, the silver(I) macrocyclic compounds containing more than two silver(I) nuclei have been rarely reported; Lehn [11] and Luo [12] obtained several polynuclear silver(I) macrocyclic compounds. So far no systematic study on silver(I) complexes with polyazamacrocycles and different anions have been reported, thus the coordination chemistry and molecular recognition of polyazamacrocycles on silver(I) ion is not yet well understood. This fact may possibly be attributed to the poor solubility of silver(I) compounds in common solvents and the sensitivity toward photodecomposition. However, as a heavy metal ion with d^{10} configuration, silver(I) exhibits rich coordination chemistry; many factors, such as the nature of the ligands, solvents, anions, *etc.*, appear to have influences on the stereochemistry and stoichiometry of silver(I) compounds [13-15]. We have therefore designed to synthesize some silver(I) complexes with a 26-membered hexaazamacrocyclic Schiff Base *L* (Scheme 1) and different counter anions, and have succeeded in obtaining some silver(I) complexes of the macrocycle *L* ligand bearing NO_3^-, ClO_4^-, PF_6^-, $PhCO_2^-$, and $MeCH(OH)CO_2^-$ as counter anions. Our results demonstrate that the counter anions play a very important role in the formation of the silver(I) compounds from the reaction mixtures, and varied counter anions lead to different products with varied metal-ligand molar ratios and different nucleations.



SCHEME 1 Structure of *L*.

2. EXPERIMENTAL

2.1. Preparations

Reagents and solvents used were of commercially available reagent quality. The macrocyclic Schiff base (*L*) was prepared by the (2+2) condensation of terephthalaldehyde with 3-azapentane-1,5-diamine according to the literature procedure [16].

2.1.1. *[Ag$_2$L(NO$_3$)$_2$] 1*

A solution of $AgNO_3$ (0.17 g; 1 mmol) in MeCN (5 mL) was added to a stirred solution of *L* (0.2 g; 0.5 mmol) in MeOH (2 mL). Slow diffusion of diethyl ether into the resulting solution for 24 h yielded colorless crystals, which were collected by filtration, washed with MeCN and MeOH and dried in a vacuum desiccator over silica gel.

2.1.2. *[Ag$_2$L(NO$_3$)$_2$]* 2

A solution of $AgNO_3$ (0.17 g; 1 mmol) in MeCN (5 mL) was added to a stirred solution of *L* (0.2 g; 0.5 mmol) in MeOH (2 mL). The mixture was sealed for a week and the yellowish crystals deposited were collected by filtration, washed with MeCN and MeOH and dried in a vacuum desiccator over silica gel.

2.1.3. *$[Ag_3L_2(NO_3)_2](ClO_4)$ 3*

A solution of $AgNO_3$ (0.17 g; 1 mmol) in MeCN (5 mL) was added to a stirred solution of *L* (0.2 g; 0.5 mmol) in MeOH (2 mL). A few minutes latter $NaClO_4$ (0.2 g) in MeOH (0.5 mL) was dropwise added to the mixture. Slow diffusion of diethyl ether into the resulting solution for 24 h produced colorless crystals, which were collected by filtration, washed with MeCN and MeOH and dried in a vacuum desiccator over silica gel.

2.1.4. *$[Ag_2L_2]PF_6$ 4*

A solution of $AgNO_3$ (0.17 g; 1 mmol) in MeCN (5 mL) was added to a stirred solution of *L* (0.2 g; 0.5 mmol) in MeOH (2 mL). A few minutes latter $NaPF_6$ (0.2 g) in MeOH(1.0 mL) was dropwise added to the mixture. Slow diffusion of diethyl ether into the resulting solution for 24 h produced colorless crystals, which were collected by filtration, washed with MeCN and MeOH and dried in a vacuum desiccator over silica gel.

2.1.5. *$[Ag_4L(MeCH(OH)CO_2)_4]$ 5*

A solution of *L* (0.2 g; 0.5 mmol) in MeOH (2 mL) was added to a stirred suspension solution of silver(I) lactate (0.4 g; 2 mmol) in MeCN (5 mL), and silver(I) lactate immediately dissolved. Upon slow diffusion of diethyl ether into the resulting solution for 24 h, pale brown crystals were deposited and collected by filtration, washed with MeCN and MeOH and dried in a vacuum desiccator over silica gel.

2.1.6. *$[Ag_4L(PhCO_2)_4]_n \bullet nAg_2(PhCO_2)$ 6*

This compound was prepared as for 5, using silver(I) benzoate, and pale yellow prismatic crystals were isolated.

All the six complexes are found stable in the air over months. The results of elemental analyses and yields for **1**–**6** are summered in Table I.

TABLE I The elemental analysis data [a] for compounds **1** to **6**

Compound	C(%)	H(%)	N(%)	Yield(%)
1	38.55(38.83)	4.07(4.07)	14.78(15.10)	75
2	39.12(38.83)	4.20(4.07)	14.90(15.10)	36
3	42.55(42.73)	4.38(4.49)	14.01(14.54)	28
4	43.98(44.03)	4.55(4.62)	12.55(12.84)	26
5	36.28(36.43)	4.13(4.25)	6.87(7.08)	46
6	44.25(44.62)	3.34(3.40)	4.43(4.73)	55

[a] Calculated values are given in parentheses.

Safety Notes *Metal perchlorate containing organic ligands are potentially explosive. Only a small amount of material should be prepared and handled with great care.*

2.2. Measurements

The C, H and N elemental analyses were carried out with a Perkin-Elmer 240Q elemental analyzer. The cyclic voltammograms were measured on electrochemical analyzer over 2.0 to − 2.0 V at room temperature, with the sample concentration of 1.0×10^{-4} $mol{\cdot}L^{-1}$ in MeCN solution containing $Bu^n{}_4NPF_6$ ($0.1\ mol{\cdot}L^{-1}$) and the scan speed of $100\ mV{\cdot}s^{-1}$. A platinum wire working electrode, a platinum plate auxiliary electrode and a saturated calomel electrode (SCE) reference electrode were employed. All potentials were measured with respect to SCE and the experiments were carried out at ca. 20°C.

2.3. Crystallography

Diffraction intensities for complexes **1**–**6** were collected at 293(2) *K* on a Siemens *R3m* diffractometer using Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å). *Lp* and absorption corrections were applied [17]. The structure solutions and full-matrix least-squares refinements based on F^2 were performed with the SHELXS-97 and SHELXL-97 program packages, respectively [18, 19]. The Ag(2) atom in **3**, being equivalently distributed over two positions related to an inversion center in the lattice, is assigned s.o.f. of 1/2. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated geometrically and allowed to ride on their parent carbon and nitrogen atoms. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [20]. The crystallographic data for all the complexes are summarized in Table II. Selected bond distances and angles are given in Table III (for **1** and **2**) and Table IV (for **3**-**6**). Additional crystallographic data are available as supplementary data.

3. RESULTS AND DISCUSSION

3.1. Structural Descriptions

3.1.1. *[$Ag_2L(NO_3)_2$]* 1

1 is an electrically neutral compound as shown in Figure 1. In **1** the two centrosymmetrically related silver(I) atoms, being separated at 6.712 (6) Å, are ligated by a macrocyclic *L* ligand. Each of the two silver(I) atoms, being situated outward in the opposite positions of the macrocycle, is coordinated by three nitrogen atoms from the macrocycle and two oxygen atoms from the bidentate nitrate group to form an irregular five-coordination geometry, being given rise by the geometric restraints of both macrocycle and nitrate ligands. The Ag—N (imine) bonds Ag(1)—N(1) = 2.331(6) and Ag(1)—N(3) = 2.311(6)Å are significantly longer than those (Ag—N = 2.126 - 2.161 Å) in a other macrocyclic Schiff Base complex [12]. All the amine nitrogen atoms in the macrocycles in **1**~**6** participate in coordination, with the Ag—N(amine) distances being slightly longer than the related Ag—N(imine) distances. The nitrate group acts in an unsymmetric chelating mode in coordination to the silver(I) atom, with Ag—O(nitrate) = 2.552(5) and 2.465(5) Å, which are significantly longer than those [Ag—O(nitrate) = 2.248(2) and 2.41(1) Å] of the [$Ag(NO_3)_2]^-$ anion found in the double metal salt [$Rh(py)_4Cl$] [$Ag(NO_3)_2$] [21], where the nitrate groups act in the unsymmetric chelating mode; but are slightly shorter than those [$Ag—O(nitrate)_3$ 2.524(3) and 2.619(3) Å] in [$Ag_2(Et_3BET)_2(NO_3)_2$] [22].

3.1.2. *[$Ag_2L(NO_3)_2$]* 2

An ORTEP plot of the molecular structure of **2** is depicted in Figure 2. **2** is centrosymmetric, with Ag...Ag separation of 6.642(2) Å. The silver(I) atom is four-coordinated by three nitrogen atoms from the Schiff Base and one oxygen atom from the monodenate nitrate group in a highly distorted tetrahedral geometry, with Ag—N(imine) bonds ranging from 2.266(4) to 2.296(3) Å and the most distroted bond angle N(1)—Ag(1)—N(2) being 75.78(12)°, which is given rise by the geometric restraints of the macrocycle ligand, as being found in **1**. Due to the monodentate ligation, the Ag—O (nitrate) bond length (2.424(3) Å) is slightly shorter than those of Ag—O(nitrate) bonds in **1**, and is comparable with that [Ag—O(nitrate) = 2.434(3) Å] in [$Ag(C_5H_5NCH_2CO_2)(NO_3)$]^{23} with a monodentate nitrate group.

1 and **2** are a pair of isomers. Although isomerism of coordination compounds is a widely known phenomenon, no such isomers as that the metal atoms are accommodated in a macrocycle have been reported. Each macrocycle in both isomers **1** and **2** adopts a chair conformation, which is apparently unstrained, as indicated by the normal and comparable bond parameters (see Tab. III). The structurally significant difference between the isomers results from the coordination fashions of the nitrate groups, which act in bidentate chelate mode in **1** and monodentate mode in **2**. Bidentate chelate mode is rarely observed for silver(I) nitrates [23, 24], because such mode experiences steric strain; therefore **1** is relatively unstable in comparison to **2**. This assumption is in accord with the fact that, with the same starting materials, rapid crystallization by diffusion of ethyl ether into the reaction mixture yielded **1** as product, whereas slower crystallization of the reaction mixture produced **2**.

TABLE II Crystal data [a] for 1–6

Compound	**1**	**2**	**3**	**4**	**5**	**6**
formula	$C_{24}H_{30}Ag_2N_8O_6$	$C_{24}H_{30}Ag_2N_8O_6$	$C_{48}H_{60}ClAg_3N_{14}O_{10}$	$C_{48}H_{60}Ag_2F_{12}N_{12}P_2$	$C_{36}H_{50}Ag_4N_6O_{12}$	$C_{66}H_{60}Ag_6N_6O_{12}$
fw	742.30	742.30	1352.16	1310.76	1190.30	1776.44
space group	$P\bar{1}$	$P2_1/n$	$C2/m$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a(Å)	7.705(7)	7.714(3)	14.950(6)	10.066(3)	13.851(9)	10.896(9)
b(Å)	7.926(5)	14.491(7)	13.258(3)	9.846(5)	8.043(3)	10.990(3)
c(Å)	12.06(1)	11.821(6)	13.832(5)	27.40(2)	19.65(1)	13.25(1)
α(deg)	90.33(1)	90	90	90	90	75.88(1)
β(deg)	95.13(1)	98.99(1)	109.15(1)	92.81(8)	107.73(2)	87.60(1)
γ(deg)	104.07(1)	90	90	90	90	82.91(1)
V(Å^3)	711(1)	1305(1)	2589(2)	1712(2)	2085(2)	1527(2)
Z	1	2	2	4	2	3
γ(MoKα)(Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T(K)	293	293	293	293	293	293
ρ(g/cm^3)	1.733	1.884	1.734	1.605	1.896	1.934
μ(MoKα) (cm^{-1})	1.430	1.558	1.247	1.778	1.918	1.956
$R_1(I > 2\sigma(I))$ [a]	0.065	0.041	0.055	0.066	0.044	0.051
wR_2 (all data) [a]	0.149	0.110	0.102	0.115	0.083	0.118

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

TABLE III Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

	1	**2**
Ag(1)—N(3)	2.311(6)	2.296(3)
Ag(1)—N(1)	2.331(6)	2.266(4)
Ag(1)—N(2)	2.386(5)	2.437(3)
Ag(1)—O(2)	2.465(5)	
Ag(1)—O(1)	2.552(5)	2.424(3)
N(3)—Ag(1)—N(1)	137.6(2)	141.2(1)
N(3)—Ag(1)—N(2)	77.2(2)	77.0(1)
N(1)—Ag(1)—N(2)	75.3(2)	75.7(1)
N(3)—Ag(1)—O(2)	108.5(2)	
N(1)—Ag(1)—O(2)	109.2(2)	
N(2)—Ag(1)—O(2)	104.7(2)	
N(3)—Ag(1)—O(1)	112.4(2)	102.7(1)
N(1)—Ag(1)—O(1)	106.7(2)	115.4(1)
N(2)—Ag(1)—O(1)	153.3(2)	144.4(1)
O(2)—Ag(1)—O(1)	48.98(2)	

TABLE IV Selected bond lengths (Å) and angles (°) for complexes **3**–**6**

		3[a]	
Ag(1)—O(1)	2.315(6)	Ag(1)—N(2a)	2.343(5)
Ag(1)—N(2)	2.343(5)	Ag(1)—N(1)	2.403(5)
Ag(2)—Ag(2b)	2.516(3)	Ag(2)—N(4)	2.174(6)
Ag(2)—N(4b)	2.361(6)	Ag(2)—N(3a)	2.530(4)
Ag(2)—N(3)	2.530(4)		
O(1)—Ag(1)—N(2)	112.2(1)	N(2a)—Ag(1)—N(2)	135.4(2)
O(1)—Ag(1)—N(1)	129.4(2)	N(2a)—Ag(1)—N(1)	76.1(1)
N(2)—Ag(1)—N(1)	76.1(1)	N(4)—Ag(2)—N(4b)	141.2(1)
N(4)—Ag(2)—N(3a)	73.4(1)	N(4b)—Ag(2)—N(3a)	117.3(1)
N(4)—Ag(2)—N(3)	73.4(1)	N(4b)—Ag(2)—N(3)	117.3(1)
N(3a)—Ag(2)—N(3)	123.5(2)		
		4[b]	
Ag(1)—N(5a)	2.260(8)	Ag(1)—N(3)	2.340(9)
Ag(1)—N(2)	2.378(8)	Ag(1)—N(1)	2.430(9)
N(5)—Ag(1a)	2.260(8)	(5a)—Ag(1)—N(3)	133.6(3)
N(5a)—Ag(1)—N(2)	119.1(3)	N(3)—Ag(1)—N(2)	76.1(3)
N(5a)—Ag(1)—N(1)	119.0(3)	N(3)—Ag(1)—N(1)	107.2(3)
N(2)—Ag(1)—N(1)	73.8(3)		
		5	
Ag(1)—O(2)	2.173(3)	Ag(1)—N(2)	2.248(3)
Ag(1)—N(1)	2.472(4)	Ag(1)—Ag(2)	3.052(1)
Ag(2)—N(3)	2.177(4)	Ag(2)—O(5)	2.280(3)
Ag(2)—O(1)	2.293(3)		
O(2)—Ag(1)—N(2)	166.2(1)	O(2)—Ag(1)—N(1)	117.2(1)
N(2)—Ag(1)—N(1)	76.5(1)	O(2)—Ag(1)—Ag(2)	81.47(9)
N(2)—Ag(1)—Ag(2)	86.6(1)	N(1)—Ag(1)—Ag(2)	144.06(9)
N(3)—Ag(2)—O(5)	144.1(1)	N(3)—Ag(2)—O(1)	133.9(1)
O(5)—Ag(2)—O(1)	81.9(1)	N(3)—Ag(2)—Ag(1)	68.25(9)
O(5)—Ag(2)—Ag(1)	137.96(8)	O(1)—Ag(2)—Ag(1)	71.7(1)
		6[c]	
Ag(1)—O(31)	2.208(5)	Ag(1)—O(32a)	2.240(6)
Ag(1)—O(22)	2.434(6)	Ag(1)—Ag(1a)	2.984(2)
Ag(1)—Ag(2)	3.060(1)	Ag(2)—O(21)	2.193(5)
Ag(2)—N(2)	2.334(7)	Ag(2)—N(3)	2.366(7)
Ag(2)—N(1)	2.475(7)	Ag(3)—O(42b)	2.155(6)
Ag(3)—O(41)	2.161(6)	Ag(3)—Ag(3b)	2.859(2)
O(32)—Ag(1a)	2.240(6)	O(42)—Ag(3b)	2.155(6)
O(31)—Ag(1)—O(32a)	153.0(2)	O(31)—Ag(1)—O(22)	125.1(2)
O(32a)—Ag(1)—O(22)	81.5(2)	O(21)—Ag(2)—N(2)	156.3(2)
N(2)—Ag(2)—N(3)	76.5(2)	O(21)—Ag(2)—N(3)	117.8(2)
N(2)—Ag(2)—N(1)	74.9(3)	O(21)—Ag(2)—N(1)	111.8(2)
O(42b)—Ag(3)—O(41)	162.6(2)	N(3)—Ag(2)—N(1)	114.1(3)

[a] Symmetry transformations: (a) $x, -y, z$; (b) $-x, -y, -z-1$.

[b] Symmetry transformations: (a) $-x+2, -y+1, -z$.

[c] Symmetry transformations: (a) $-x, -y+1, -z$; (b) $-x, -y, -z$; (c) $1-x, -y, -z$.

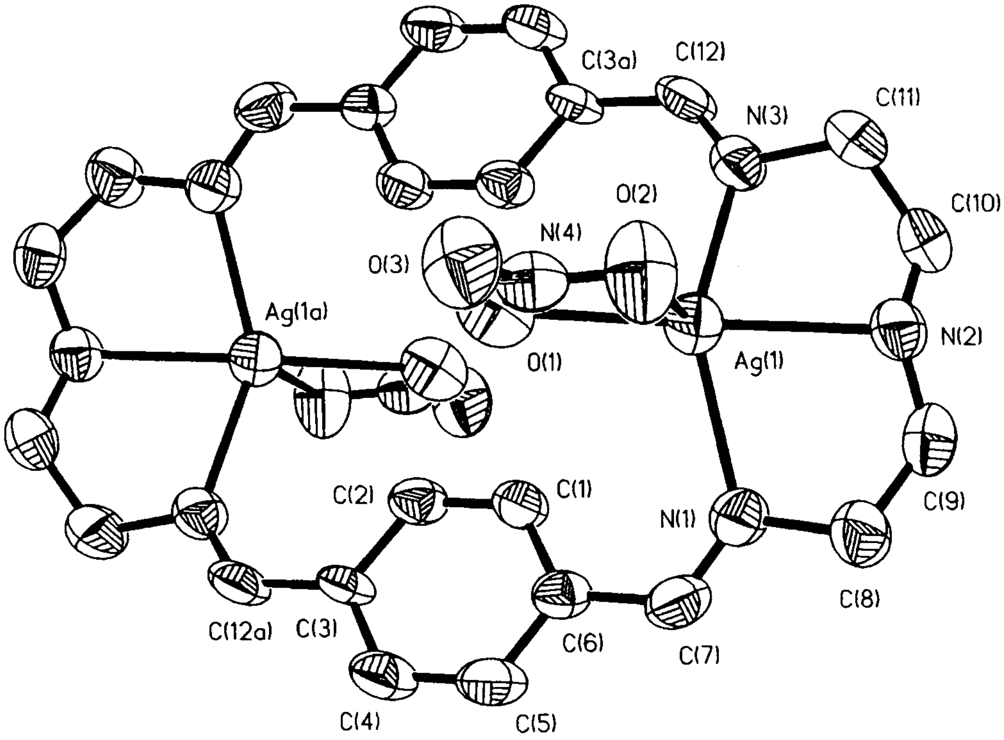


FIGURE 1 ORTEP view (at the 35% probability level) of 1. The hydrogen atoms are omitted.

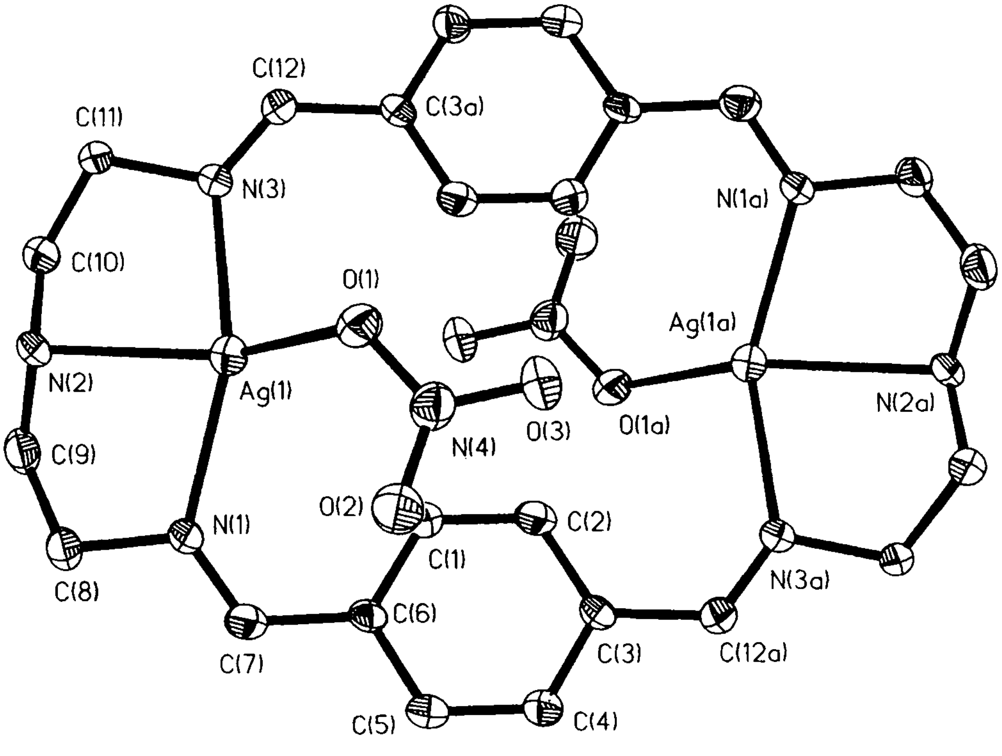


FIGURE 2 ORTEP view (at the 35% probability level) of 2. The hydrogen atoms are omitted.

3.1.3. *[$Ag_3L_2(NO_3)_2$](ClO_4) 3*

The structure of **3** consists of discrete silver(I)-linked trinuclear [$Ag_3L_2(NO_3)_2$]$^+$ cations and perchlorate anions, as shown in Figure 3. Crystallographically, the trinuclear [Ag_3L_2 $(NO_3)_2$]$^+$ cation in **3** is centrosymmetric, and has a mirror plane passing through atoms Ag(1), Ag(2), O(1), O(2), O(3), N(5), N(1) and N(4). It should be noted that the central metal atom Ag(2) is equivalently distributed over two positions related by the inversion center, and at each position the half-occupied silver(I) atom is tetrahedrally coordinated by three nitrogen atoms (Ag—N(imine) = 2.530(4), Ag—N(amine) = 2.174(6)Å) from one macrocycle and one amine nitrogen atom (Ag—N = 2.361(6) Å) from the inversely-related macrocycle. Therefore, the coordination geometry for the Ag(2) atom at each of the two positions is equivalent, and only one is shown in Figure 3. At each side of this trinuclear cation, the Ag(1) atom is also tetrahedrally coordinated by three nitrogen atoms from a macrocycle and one oxygen atom from a monodentate nitrate group. The coordination polyhedron of the Ag(1) atom, similar to that of the Ag(2) atom, is highly distorted, given rise by the geometric restraint of the ligand. The average Ag—N(imine) bond (2.343(5) Å) and the Ag—N(amine) bond lengths (2.403(5) Å) are close to those in other complexes reported in this paper. The Ag—O distance (Ag(1)—O(1) = 2.315(6)Å) is significantly shorter than that (Ag—O = 2.424(3) Å) in **2**, indicating a stronger silver-oxygen interaction, which may be ascribed to that the two nitrates in **3** are situated at the opposite sides of the macrocycles and having no significant steric interaction. No analogous trinuclear structure has been reported for the related silver(I) marcocycle compounds so far.

3.1.4. *[Ag_2L_2] PF_6 4*

The complex consists of a discrete centrosymmetric [Ag_2L_2]$^{2+}$ cation and two PF_6^- anions. As shown in Figure 4, two metal atoms are wrapped by a pair of the macrocyclic ligands in the dimeric cation. Each metal atom adopts a distorted tetrahedral coordination geometry, being ligated by three nitrogen atoms N(1), N(2) and N(3) from a macrocycle, and one amine nitrogen atom N(5a) atom from another macrocycle. To our knowledge, this is the first example that two dinucleating macrocyclic Schiff Base ligands are connected together by a pair of metal atoms. The average Ag—N(imine) bond length (2.340 Å) in **4** is much longer than those (Ag—N = 2.126 – 2.161 Å) in the other

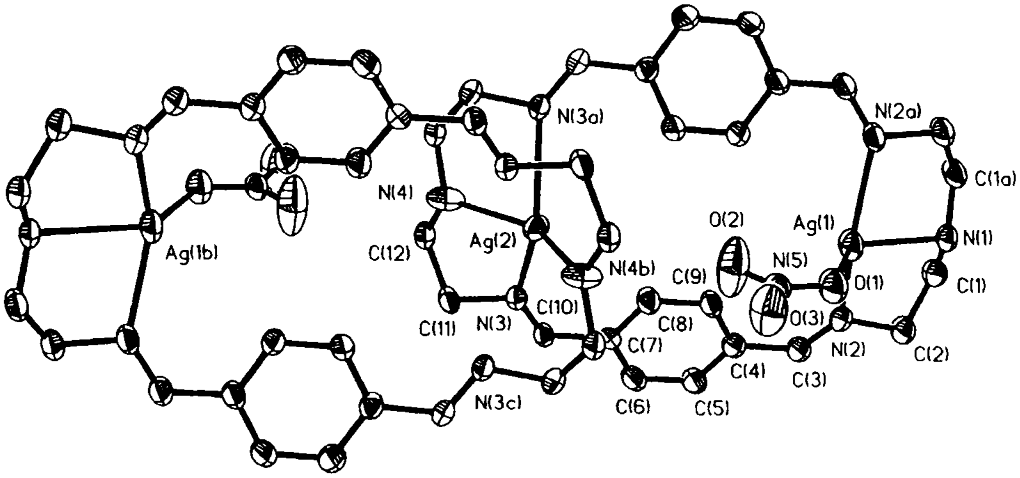


FIGURE 3 ORTEP view (at the 35% probability level) of the trinuclear cation in 3. The hydrogen atoms are omitted.

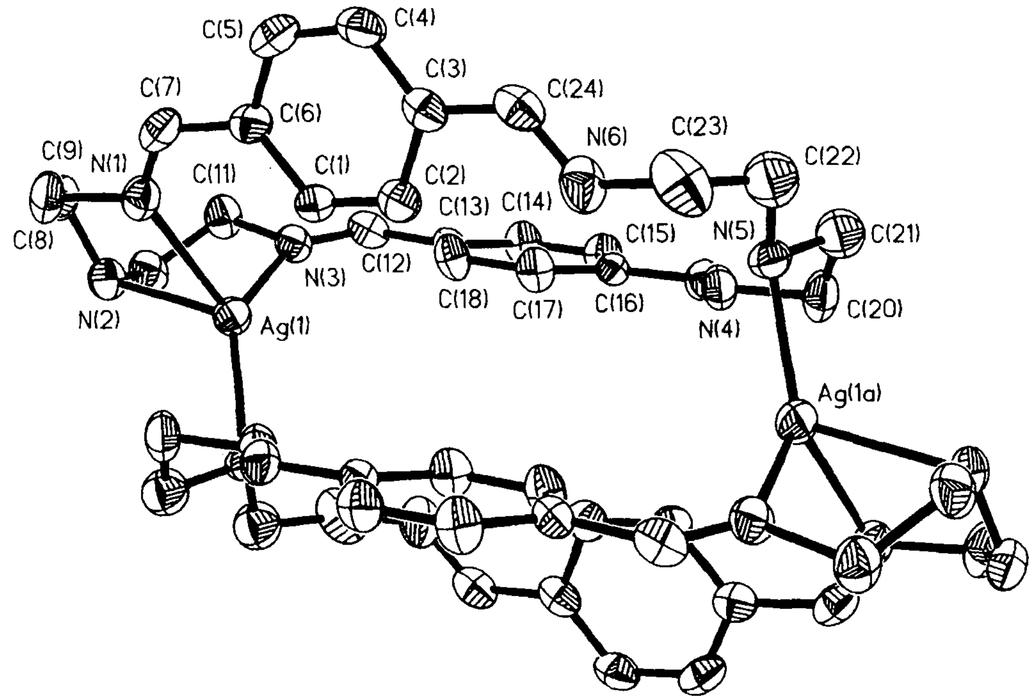


FIGURE 4 ORTEP view (at the 35% probability level) of the dinuclear cation in 4. The hydrogen atoms are omitted.

macrocyclic Schiff Base complex [12], thus indicating a weaker Ag—N interaction. Each macrocycle in 4 is almost fully extended and has no unusual bond lengths or angles.

3.1.5. *$[Ag_4L(MeCH(OH)CO_2)_4]$ 5*

As illustrated in Figure 5, 5 is a discrete centrosymmetric tetranuclear complex comprising two dinuclear cores, in which the carboxylate groups serve in monodentate and bridging modes. The pair of silver(I) atoms bridged by a single μ_2-carboxylate group of lactate in a dinuclear core are separated at 3.053(1) Å, being significantly larger than that (2.89 Å) in metallic silver, which indicates very weak metal-metal interaction. The geometry of both Ag(1) and Ag(2) atoms are in distorted trigonal fashions in each dinuclear core. However, the Ag(1) atom is in a *T*-shape fashion (N(2)—Ag(1)—N(1) = 76.5(1), O(2)—Ag(1)—N(1) 117.3(1) and O(2)—Ag(1)—N(2) = 166.2(1)°) with coordination of two nitrogen atoms from the macrocycle and a carboxy oxygen atom from a μ_2-lactate, and the Ag(2) atom is in a *Y*-shape fashion (O(5)—Ag(2)—O(1) = 81.9(1), N(3)—Ag(2)—O(1) = 133.9(1) and N(3)—Ag(2)—O(5) = 144.1(1)°) with coordination of two different carboxy groups and an imine nitrogen atom. The Ag—O(carboxy) bonds (2.173(3) to 2.293(3) Å) are comparable to those reported in silver(I) carboxylates [24], while the Ag—N bond lengths in 5 are also similar to those reported in this work. It is worthy of note that although crystal structures of silver(I) carboxylates have been well documented, monodentate carboxylate mode is rarely reported, one analogous example being recently uncovered [25]. The metal-carboxylate fragments of the two dinuclear cores in 5 are inversely-related and situated at the opposite side of the macrocycle, displaying a *trans*-conformation. The intra-macrocyclic Ag(1)...Ag(1a) separation (6.262(6) Å) in 5 is much shorter than the corresponding values in 1

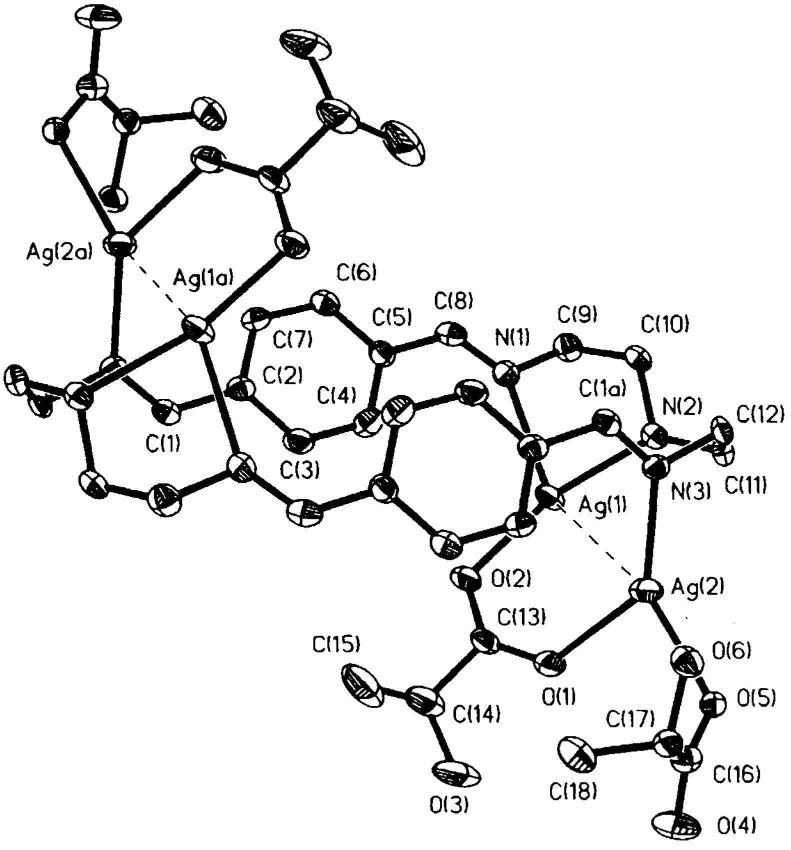


FIGURE 5 ORTEP view (at the 35% probability level) of 5. The hydrogen atoms are omitted.

(6.712(6) Å) and in **2** (6.642(6) Å), implying that the macrocycle is slightly folded in **5**.

3.1.6. $[Ag_4L(PhCO_2)_4]_n \bullet nAg_2(PhCO_2)_2$ 6

The crystal structure of **6** comprises infinite one-dimensional $[Ag_4L(PhCO_2)_4]_n$ chains and the discrete dimeric $Ag_2(PhCO_2)_2$ species. In the polymeric chain, each macrocycle *L* ligand binds two inversely-related silver(I) atoms in a *trans* conformation, as is shown in Figure 6. Except the three nitrogen atoms from the macrocycle *L* ligand (average Ag—N = 2.39Å), the Ag(2) atom is further ligated by an oxygen atom from a μ_2-benzoate group (Ag(2)—O(21) = 2.193 (5)Å), resulting in a distorted tetrahedral coordination geometry; this μ_2-benzoate group bridges the Ag(2) atom to a bis(μ_2-benzoate)disilver(I) dimeric core, extending the structure into a neutral one-dimensional polymer running along the *b*-axis in solid. Therefore, there are two kinds of μ_2-carboxylate bridges, *i.e.*, single and double μ_2-carboxylate bridges, in each $[Ag_4L(PhCO_2)_4]$ repeating unit in the polymeric chain. The bis(μ_2-benzoate)disilver(I) dimeric core is structurally similar to a number of silver(I) carboxylates containing dimeric structures [23, 24, 26], whereas the single carboxylate bridge is somewhat unusual since the structure of a pair of silver(I) atoms bridged by a *single* μ_2-carboxylate bridge is rarely observed [27]. More interestingly, the single μ_2-carboxylate bridge exhibits an uncommon non-coplanar skew-skew coordination mode with the torsional angles of C(22)—C(21)—O(21)—Ag(1) and C(22)—C(22)—O(21)—Ag(2) at 145 and 11°, respec-

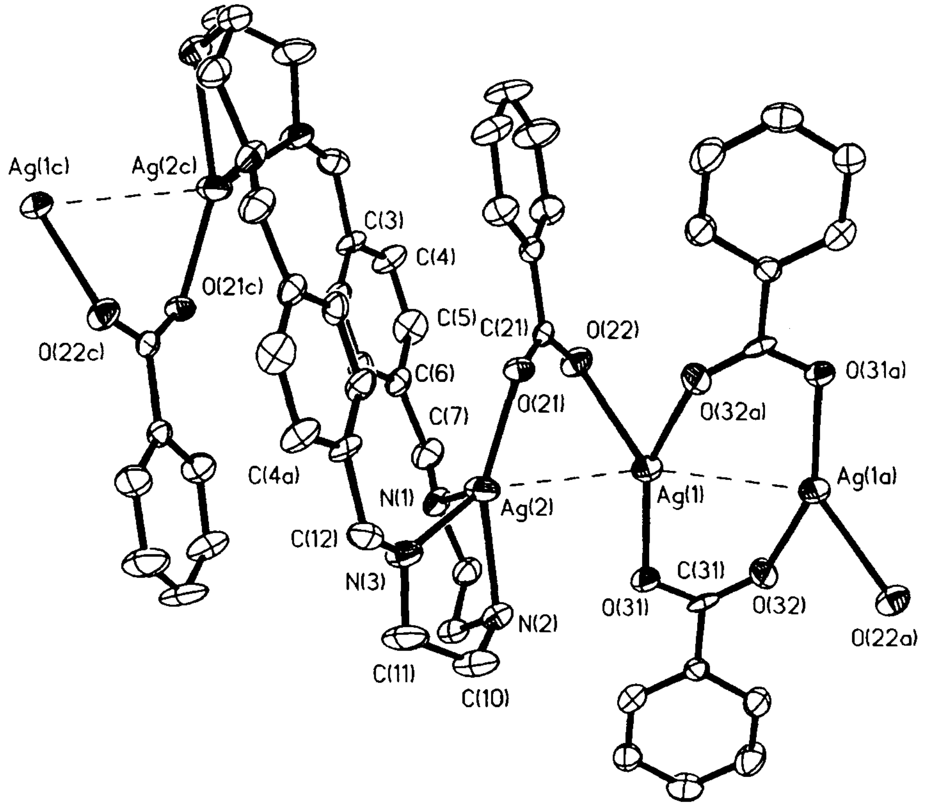


FIGURE 6 (a) ORTEP view showing a repeating unit of the polymeric chain in 6.

tively; similar phenomenon has been reported in our previous studies of cadmium(II) and manganese(II) carboxylates [28]. The centrosymmetric macrocycle adopts full-stretched chair conformation with the largest intra-macrocyclic Ag…Ag separation (Ag(2)…Ag(2c) = 7.004(6) Å) as compared to those in metal complexes of a 24-membered hexaazamacrocyclic Schiff Base. Each pair of adjacent silver(I) atoms in the tetranuclear subunit is separated a distance (Ag(1)…Ag(1a) = 2.984(2), Ag(1)…Ag(2)=3.061 (2)Å) slightly longer than the intradimeric metal-metal contact [2.92(1) Å] in the crystal structure of [Ag$_2$(PhCO$_2$)$_2$] [29]. The four metal atoms (Ag(2)—Ag(1)—Ag(1a)—Ag(2a)) are arranged in approximately linear fashion (Ag(1a)—Ag(1) — Ag(2) = 157.85(6)°), similar structural motif is seldom seen for silver(I) complexes although it is usual in platinum (II, III) complexes [23, 24].

The discrete dimeric Ag$_2$(PhCO$_2$)$_2$ species in **6** is structurally very similar to the simple [Ag$_2$(PhCO$_2$)$_2$] [29], although the intradimeric Ag…Ag separation (Ag(3)…Ag(3b) = 2.859(2) Å) in the former is slightly shorter than that (2.92(1) Å) in the later. The discrete dimeric Ag$_2$(PhCO$_2$)$_2$ species are inserted into the cavities constructed by the polymeric chains in **6**, and interact with the chains through metal-oxygen contacts between the discrete Ag$_2$(PhCO$_2$)$_2$ species and the chains (Ag(3)—O(21) = 2.590(6)Å and Ag(3)—O(32a) = 2.817(6)Å), as well as the $\pi-\pi$ stacking interaction between the phenyl rings (the face-to-face distance is ca 3.7 Å) of the discrete [Ag$_2$(PhCO$_2$)$_2$] species and the chains, as illustrated in Figure 6b. This weak interactions furnish a two-dimensional network perpendicular to the *c*-axis.

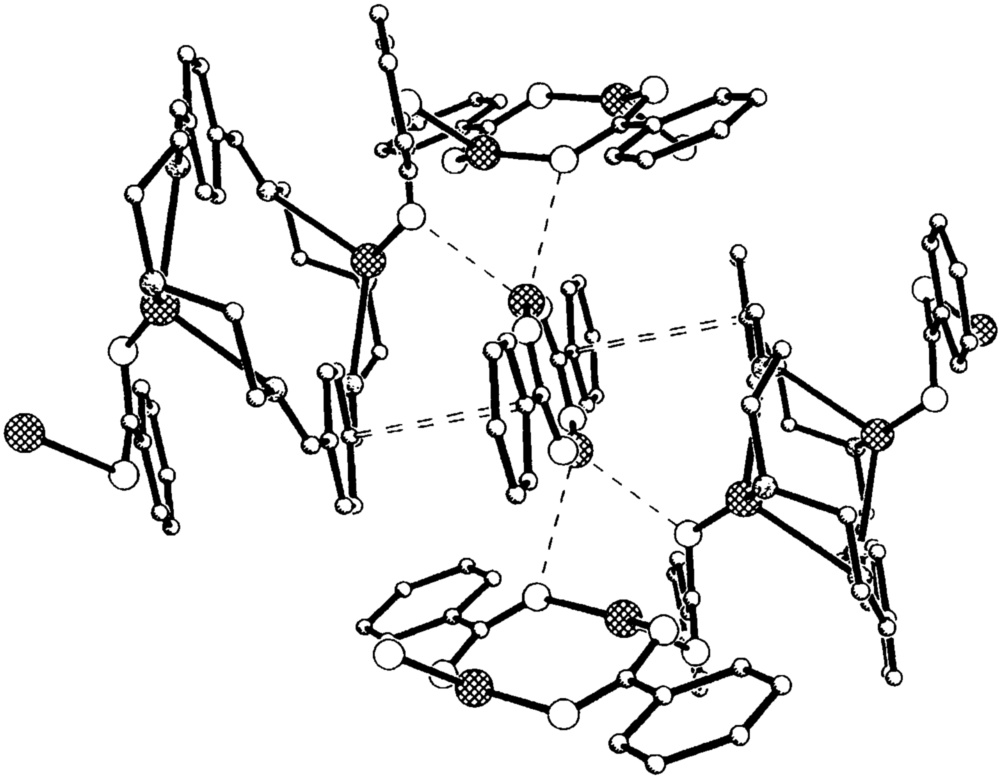


FIGURE 6 (b) Perspective view showing the discrete $Ag_2(PhCO_2)_2$ species enclosed with the cavity formed by the polymeric chains in **6**.

3.2. Effects of Anions on the Formation of the Complexes

Commonly the 26-membered hexaazamacrocyclic Schiff Base *L* (See Scheme I) can be expected to function as a dinucleating ligand with each binding site utilizing three nitrogen atoms as donors, and the *p*-xylyl linker groups are rigid enough to preclude it from mononuclear complexion. Although silver(I) atom is very flexible in coordination, coordination of the three nitrogen atoms at each binding site will usually be unsaturated. Therefore, each silver(I) atom in both **1** and **2** still requires ligation of a nitrate group acting in either monodentate or bidentate chelate. Hence the disilver(I) nitrates **1** and **2** were easily obtained by reacting silver(I) nitrate with *L* in MeCN solution. It is notable that nitrate is a very weak donor in coordination to a silver(I) atom, and may be easily removed in the presence of other ligands or counter anions, such as ClO_4^- and PF_6^-. Although the later two anions are both weaker donors than nitrate, their salts of silver(I) complexes are usually poorer in solubility. After removal of the ligated nitrate group, the silver(I) atom will be unsaturated in coordination, and requires additional donor from another macrocyclic Schiff Base. Therefore, when excess large anions, such as ClO_4^- and PF_6^-, are added to the solution containing $AgNO_3$ and *L*, the coordinated nitrate groups may be replaced at a certain degree, depending on the solubility of the corresponding product, to form **3** and **4**, respectively.

Carboxylate ligands have strong tendency to bridge silver(I) atoms to construct polymeric species, as being well-documented [22–24, 26]. This bridging behavior leads to the formation of **5** and **6**, in which the carboxylate ligands do promote polymerization *via* μ_2-carboxylate bridges.

Although the preparations of **1**–**6** need not to be performed under an inert atmosphere and degassed solvents, these complexes could not be obtained from aqueous solution. In order to obtain the crystalline products of the complexes at high yield, long reaction time and high temperature must be avoided. When the reaction mixture was heated to 50°C for 5 mins, only the viscous was obtained.

3.3. Electrochemistry

The redox potentials of the six complexes are presented in Table V, while voltammograms (CV) are deposited as supplementary data. The cathodic wave at −0.750 V and anodic waves at 1.600 V for each compound has been confirmed to be associated with the macrocycle *L* ligand by the redox potentials of the free ligand.

3.3.1. $[Ag_2L(NO_3)_2]$ *1 and 2*

The electrochemical behaviors of **1** and **2** are the same, implying that the coordination geometry of the metal atoms in solution are the same. The CV of **1** shows five redox waves. The cathodic waves centred at −0.075 and −0.125 V may be assigned respectively to the reactions $[Ag^IAg^IL(NO_3)_2]^0 + e \rightarrow [Ag^IAg^0L(NO_3)_2]^-$ and $[Ag^IAg^0L(NO_3)_2]^- + e \rightarrow [Ag^0Ag^0L(NO_3)_2]^{2-}$, since the peak current ratio of the cathodic waves was about 1:1. Because the peak current ratio of the cathodic wave at −0.125 V and the anodic wave at 0.425 V was about 1:2, the anodic wave may be assigned to $[Ag^0Ag^0L(NO_3)_2]^{2-} - 2e \rightarrow [Ag^I\,Ag^IL(NO_3)_2]^0$ in one step.

3.3.2. $[Ag_3L_2(NO_3)_2](CLO_4)$ *3*

The CV of **3** shows cathodic waves occurring at −0.125 V and −0.425 V with the peak current ratio of the cathodic waves of ca. 1:2, suggesting the reactions, $[Ag^IAg^IAg^IL_2(NO_3)_2]^+ + e \rightarrow [Ag^IAg^IAg^0L_2(NO_3)_2]^0$ and $[Ag^IAg^IAg^0L_2(NO_3)_2]^0 + 2e \rightarrow [Ag^0Ag^0Ag^0L_2(NO_3)_2]^{2-}$. Because the peak current ratio of the cathodic wave at −0.125 V and the anodic wave at 0.425 V was about 1:3, the anodic wave may be assigned to $[Ag^0Ag^0Ag^0L_2(NO_3)_2]^{2-} - 3e \rightarrow [Ag^IAg^IAg^IL_2(NO_3)_2]^+$ in one step. The electrode process is quite unusual to lose 3 electrons in one step.

3.3.3. $[Ag_2L_2]PF_6$ *4*

The cathodic waves occur with the reduction peak at −0.125 V and −0.425 V with the peak current ratio of the cathodic waves of ca. 1:1, which indicates formation of two valence states, $[Ag^IAg^0L_2]^+$ and $[Ag^0Ag^0L_2]^0$, respectively. Because the peak current ratio of the cathodic wave at −0.125 V and the anodic wave at 0.425 V was about 1:2, the anodic wave may be assigned to $[Ag^0Ag^0L_2]^0 - 2e \rightarrow [Ag^IAg^IL_2]^{2+}$ in one step.

3.3.4. $[Ag_4L(MeCH(OH)CO_2)_4]$ *5*

The cathodic wave at −0.020 V and the anodic wave at 0.090 V is a couple of reversible charge transfer processes. For the reversible charge transfer, the peak and half-peak potentials have the following relation: $|E_p - E_{p/2}| = 2.2RT/nF$ (Eq. 1) [30]. From the data of $|E_p - E_{p/2}|$ and Eq. 1, the electron transfer number of the reduction peak at −0.020 V was determined to 2.

TABLE V The CV data of complexes **1**–**6** in MeCN at room temperature

Compound	$E_{p,c}$				$E_{p,a}$		
L	−0.750						1.600
1 and 2	−0.750		−0.125	−0.075		0.425	1.600
3	−0.750	−0.425	−0.125			0.425	1.600
4	−0.750	−0.450	−0.125			0.425	1.600
5	−0.750	−0.400		−0.020	0.09	0.425	1.600
6	−0.750	−0.450	−0.200	−0.020	−0.120	0.425	1.600

The number of electrons of the cathodic wave at -0.400 V was confirmed to be 2 by the peak current ratio of the cathodic waves was about 1:1. The cathodic waves occurring with the peak at -0.020 and -0.400 V indicates the reactions, $[Ag^IAg^IAg^IAg^I]^{4+} + 2e \rightarrow [Ag^IAg^IAg^0Ag^0]^{2+}$ and $[Ag^IAg^IAg^0Ag^0]^{2+} + 2e \rightarrow [Ag^0Ag^0\,Ag^0Ag^0]^0$, respectively. Because the peak current ratio of the cathodic wave and the anodic wave was about 1:1, the anodic waves may correspond to $[Ag^0\,Ag^0Ag^0Ag^0]^0 - 2e \rightarrow [Ag^IAg^IAg^0Ag^0]^{2+}$ and $[Ag^I\,Ag^IAg^0Ag^0]^{2+} - 2e \rightarrow [Ag^IAg^IAg^IAg^I]^{4+}$, respectively.

3.3.5. *$[Ag_4L(PhCO_2)_4]_n \bullet nAg_2(PhCO_2)_2$ 6*

The CV of **6** shows a reversible redox couple with the cathodic wave at -0.200 V and the anodic wave at -0.120 V. The electron transfer number consumed at this step was confirmed to be 2 by coulometry. The number of electrons of the cathodic waves at -0.020 and -0.450 V was confirmed to be 2 according to the peak current ratio of the cathodic waves being about 1:1. Since the polarization potential is governed by the coordination environments of metal atoms, stronger donor-coordination ability results in more negative polarization potential. Therefore the reduction peak at -0.020 V may be assigned to the reduction process of the pair of silver(I) atoms in the discrete guest $[Ag_2(PhCO_2)_2]$ species in **6**. The reduction peaks at -0.120 and -0.450 V may indicate the reactions of the fragment of the polymeric chain, $[Ag^IAg^IAg^I\,Ag^I]^{4+} + 2e \rightarrow [Ag^IAg^IAg^0Ag^0]^{2+}$ and $[Ag^IAg^I\,Ag^0Ag^0]^{2+} + 2e \rightarrow [Ag^0Ag^0Ag^0Ag^0]$, respectively. Because the peak current ratio of the anodic waves at -0.120 and 0.425 V was about 1:2, the anodic wave at -0.120 V may correspond to $[Ag^0Ag^0Ag^0Ag^0] - 2e \rightarrow [Ag^IAg^IAg^0Ag^0]^{2+}$. The anodic wave at 0.425 V is a multi-electron transfer process, and may be assigned to $[Ag^IAg^IAg^0Ag^0]^{2-} - 2e \rightarrow [Ag^IAg^IAg^IAg^I]^0$ and the oxidation of the pair of silver (0) atoms in the discrete $[Ag_2(PhCO_2)_2]$ species.

The above CV results indicate that all the six complexes are stable in the range of -0.125 to 0.425 V of CV tests in MeCN, and that they may gain one or multi-electrons when they were reduced in one or two steps depending on the coordination environments of the silver(I) atoms, and lose multi-electron when the reduced forms are oxidized in one step. Unfortunately, there is no obvious relation between the redox potentials and the crystal structures.

4. CONCLUSION

The stereochemistry and stoichiometry of silver(I) compounds of the 26-membered hexaazamacrocyclic Schiff Base can be varied by existence of different counter anions in the formation process, depending mainly on the nature of the counter anions. There is no obvious relation between the redox potentials and the crystal structures.

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