

## Supramolecular helical architecture assembled by double-helical $[Ag_2L_2]$ units

Wen-Hua Sun <sup>a,\*</sup>, Tianzhu Zhang <sup>a</sup>, Leyong Wang <sup>a</sup>, Yong Chen <sup>a</sup>, Roland Froehlich <sup>b</sup>

<sup>a</sup> State Key Laboratory of Engineering Plastics and the Center for Molecular Sciences, Institutes of Chemistry, The Chinese Academy of Science, Beijing 100080, China

<sup>b</sup> Organisch-Chemisches Institut, Westfaelische Wilhelms-Universitaet, Corrensstrasse 40, Muenster D-48149, Germany

Received 30 April 2003; accepted 18 September 2003

### Abstract

A series of new sterically hindered bridged ligand 4,4'-methylene-*N,N'*-bis(phenyl-2-pyridylmethylene)-bis(2,6-dialkylanil)s was efficiently synthesized by the condensation reaction of 4,4'-methylene-bis(2,6-disubstituted aniline) and benzoyl pyridine. They easily coordinated with Ag(I) to form Ag(I) complexes. The structure of complex  $[Ag_2L_2^4][ClO_4]_2$  was determined by the single X-ray crystallographic analysis, and the double-helical asymmetric unit containing two  $[Ag_2L_2^4]$  moieties was interconnected with the adjacent unit through hydrogen bonds to form a helical supramolecular architecture.

© 2003 Elsevier B.V. All rights reserved.

**Keywords:** Sterically hindered bridged ligand; Silver complex; Double-helices; Self assembly

### 1. Introduction

In the recent decades, metallo-supramolecular chemistry has drawn much attention and provided an important forum for the evolution of coordination chemistry and material science [1–5], and double helical supramolecular array is an attractive geometric motif in nature [5,6]. Many organometallic building blocks, especially the metal/ligand couples, are widely prepared and applied to construct sophisticated supramolecular arrays. Among the families of organic ligands, multidentate imines are renowned for the generality of their easy syntheses by simple condensation reaction of aldehyde (or ketone) with amines, as well as their inherent advantage of coordinating with metal ions to form polynuclear aggregates with considerable structural diversity. The bridged tetradentate ligands were reported to coordinate with copper (II) in affording double-helical supramolecular motif in high yield [7,8], and their analogues of the ligands were prepared and used for

same purpose [9]. The controlled formation of double or triple-helical complexes were reported on the base of multidentate imine ligands [10,11], and employing analogous imine ligand the  $[Cu_2L_2]$  helix units were further assembled to nano-scale circular supramolecular array through  $\pi$ - $\pi$  aggregation [12]. Moreover, twisted ligands assembled with suitable ions to form dinuclear helicates [13]. It would be interesting to employ silver in the relative research, and dimeric double-helical units were obtained. Herein, we report the formation of a self-assembling supramolecular architecture from the dimeric double-helical  $[Ag_2L_2^4]$  moieties ( $L^4 = 4,4'$ -methylene-*N,N'*-(phenyl-2-pyridylmethylene)-bis(2,6-diethyl-anil)).

### 2. Experimental section

#### 2.1. Materials and apparatus

All reactions were carried out under an atmosphere of nitrogen. All starting materials were commercially available from Acros and used without further purification. Solvents were refluxed over an appropriate drying

\* Corresponding author. Tel.: +86-10-62557955; fax: +86-10-62618239.

E-mail address: [whsun@iccas.ac.cn](mailto:whsun@iccas.ac.cn) (W.-H. Sun).

agent and distilled prior to use. The  $^1\text{H}$  NMR spectra were recorded on Bruker DMX-300 spectrometer. IR spectra were obtained as KBr pellets on Perkin–Elmer FT-IR 2000 Spectrometer. Mass spectra were measured on a Kratos AEI MS-50 instrument using fast atom bombardment (FAB) technology or Bruker APEX II MALDI-FT-ICRMS technology. Melting points were determined with digital electrothermal apparatus without further correction. UV–visible spectra were obtained in  $\text{CH}_2\text{Cl}_2$  on SHIMADZU UV-2501PC spectrophotometer at 298 K. Polarogram (cyclic voltammogram) was recorded on Zaher IM6e Impedance Measurement Unit at 298 K. Solvent and supporting electrolyte are  $\text{CH}_2\text{Cl}_2$  and  $(t\text{-Bu})_4\text{NClO}_4$ , respectively. The half-wave potentials refer to the aqueous saturated calomel electrode (SCE).

## 2.2. Preparation of ligands

The ligands were prepared with reported procedure (Scheme 1) [14]. Typically 4,4'-methylene-bis(2,6-disubstituted aniline) (10.0 mmol) and benzoyl pyridine (22.0 mmol) were combined with two drops of conc.  $\text{H}_2\text{SO}_4$  and  $\text{Si}(\text{OEt})_4$  (23.0 mmol) in a flask. The flask was equipped with a condenser along with a water knockout trap, and the mixture was heated at  $150\text{ }^\circ\text{C}$  under nitrogen for 10 h. The EtOH formed in the reaction was collected in the water knockout trap, and the residue was dissolved in  $\text{Et}_2\text{O}$  (50 mL) and washed with saturated aqueous  $\text{NaHCO}_3$  solution, then  $\text{H}_2\text{O}$  (25 mL each). The  $\text{Et}_2\text{O}$  solution was dried with  $\text{MgSO}_4$  and solvent removed under reduced pressure. The crude product was then purified by flash column chromatography over silica gel with the eluent of petroleum/ethyl acetate (4:1) to give pure imine.

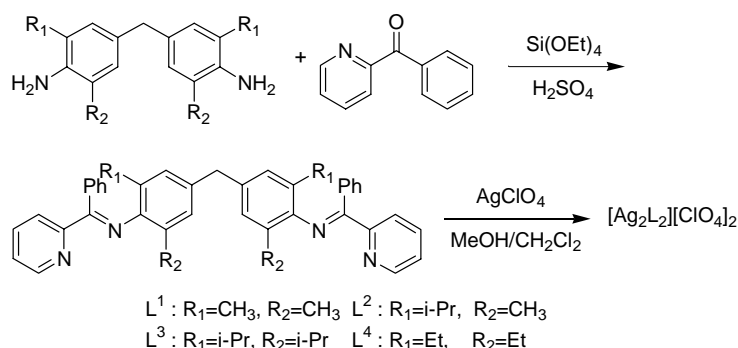
4,4'-Methylene-*N,N'*-(phenyl-2-pyridinylmethylene)-bis(2,6-dimethyl-anil) ( $\text{L}^1$ ), yellow crystals with isolated yield 65%. m.p.  $199\text{--}200\text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $\delta$  ppm): 1.97 (s, 6H), 2.02 (s, 6H), 3.65 (t, 2H), 6.61 (t, 4H), 6.95 (d, 1H), 7.10 (d, 2H), 7.14–7.25 (m, 5H), 7.37–7.49 (m, 5H), 7.78 (dd, 2H), 8.24 (d, 1H), 8.61

(d, 1H), 8.64 (d, 1H). MS (FAB,  $m/z$ ): 585 ( $\text{M}^++1$ ). Anal. Calcd. for  $\text{C}_{41}\text{H}_{36}\text{N}_4$ : C 84.21, H 6.21, N 9.58. Found: C 84.08, H 6.30, N 9.26%. IR (KBr,  $\text{cm}^{-1}$ ): 3430, 3054, 3001, 2908, 1740, 1632, 1575, 1471, 1438, 1378, 1311, 1217, 1139, 1086, 997, 961, 804, 751, 698.

4,4'-Methylene-*N,N'*-(phenyl-2-pyridinylmethylene)-bis(2-isopropyl-6-methyl-anil) ( $\text{L}^2$ ): yellow crystals, isolated yield 58%. m. p.  $162\text{--}163\text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $\delta$  ppm): 0.87 (d, 6H), 1.08 (d, 6H), 1.97 (s, 3H), 2.04 (s, 3H), 2.79–2.95 (m, 2H), 3.75 (dd, 2H), 6.61–6.80 (m, 4H), 6.95 (d, 1H), 7.09–7.22 (m, 5H), 7.39–7.47 (m, 6H), 7.79 (d, 2H), 7.84 (t, 1H), 8.24 (d, 1H), 8.60 (d, 1H), 8.65 (d, 1H). MS (FAB,  $m/z$ ): 641 ( $\text{M}^++1$ ). Anal. Calcd. for  $\text{C}_{45}\text{H}_{44}\text{N}_4$ : C 84.34, H 6.92, N 8.74. Found: C 84.36, H 7.00, N 8.35%. IR (KBr,  $\text{cm}^{-1}$ ): 3427, 3055, 2962, 2868, 1957, 1629, 1582, 1468, 1442, 1380, 1316, 1245, 1214, 1161, 1131, 1089, 994, 959, 882, 860, 797, 746, 697.

4,4'-Methylene-*N,N'*-(phenyl-2-pyridinylmethylene)-bis(2,6-diisopropyl-anil) ( $\text{L}^3$ ), yellow crystals, isolated yield 52%. m. p.  $64\text{--}65\text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $\delta$  ppm): 0.84 (d, 6H), 0.91 (d, 6H), 1.12 (d, 12H), 2.86 (t, 2H), 2.95 (t, 2H), 3.88 (dd, 2H), 6.78 (t, 4H), 6.98 (d, 1H), 7.11–7.23 (m, 5H), 7.38–7.52 (m, 6H), 7.81 (d, 2H), 7.88 (t, 1H), 8.24 (d, 1H), 8.66 (dd, 2H). MS (FAB,  $m/z$ ): 697 ( $\text{M}^++1$ ). Anal. Calcd. for  $\text{C}_{49}\text{H}_{52}\text{N}_4$ : C 84.44, H 7.52, N 8.04. Found: C 84.12, H 7.71, N 7.72%. IR (KBr,  $\text{cm}^{-1}$ ): 3420, 3057, 2962, 2930, 2867, 1964, 1740, 1627, 1583, 1567, 1493, 1465, 1382, 1361, 1334, 1317, 1300, 1281, 1247, 1211, 1156, 1074, 1047, 994, 958, 886, 862, 796, 765, 746, 696, 617.

4,4'-Methylene-*N,N'*-(phenyl-2-pyridinylmethylene)-bis(2,6-diethyl-anil) ( $\text{L}^4$ ), yellow crystals, isolated yield 73%. m. p.  $156\text{--}157\text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $\delta$  ppm): 1.07 (m, 12H), 2.19–2.26 (m, 4H), 2.39–2.59 (m, 4H), 3.78 (dd, 2H), 6.70 (t, 4H), 6.95 (d, 1H), 7.08–7.24 (m, 5H), 7.35–7.47 (m, 6H), 7.80 (d, 2H), 7.84 (t, 1H), 8.24 (d, 1H), 8.59 (d, 1H), 8.65 (d, 1H). MS (FAB,  $m/z$ ): 641 ( $\text{M}^++1$ ). Anal. Calcd. for  $\text{C}_{45}\text{H}_{44}\text{N}_4$ : C 84.34, H 6.92, N 8.74. Found: C 84.06, H 6.89, N 8.41%. IR (KBr,  $\text{cm}^{-1}$ ): 3400, 3056, 2966, 2932, 2873, 1955, 1739, 1627,



Scheme 1. Synthetic procedure for the complexes.

1582, 1462, 1371, 1315, 1243, 1212, 1169, 1138, 1090, 1049, 994, 958, 883, 856, 799, 747, 696, 662, 617.

### 2.3. Preparation of complexes

To the solution of ligand (0.12 mmol) in 10 mL MeOH/CH<sub>2</sub>Cl<sub>2</sub> (5:1) was added the solution of AgClO<sub>4</sub> (0.1 mmol) in 5 mL MeOH. The mixture was stirred overnight at room temperature. After removal of the solvent under reduced pressure, the residue was washed with Et<sub>2</sub>O to obtain the complexes (Scheme 1).

Bis[4,4'-methylene-*N,N'*-(phenyl-2-pyridinylmethlene)-bis(2,6-dimethyl-anil)] · (AgClO<sub>4</sub>)<sub>2</sub>, complex [Ag<sub>2</sub>L<sub>2</sub><sup>1</sup>][ClO<sub>4</sub>]<sub>2</sub>: brown solid, yield 84%. m.p. 157–158 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, δ ppm): 8.86 (d, 2H), 7.97 (t, 2H), 7.87 (t, 2H), 7.46 (d, 2H), 7.06–7.43 (m, 10H), 6.57 (s, 4H), 3.70 (s, 2H), 1.65 (s, 12H). Anal. Calcd. for [Ag<sub>2</sub>L<sub>2</sub><sup>1</sup>][ClO<sub>4</sub>]<sub>2</sub> · 3CH<sub>3</sub>OH: C 60.71, H 5.00, N 6.66. Found C 60.72, H 4.58, N 6.59%. IR (KBr, cm<sup>-1</sup>): 3751, 3452, 3060, 2919, 2852, 1994, 1620, 1587, 1473, 1438, 1378, 1317, 1252, 1218, 1093, 1006, 972, 922, 878, 850, 798, 747, 701, 622.

Bis[4,4'-methylene-*N,N'*-(phenyl-2-pyridinylmethlene)-bis(2-isopropyl-6-methyl-anil)] · (AgClO<sub>4</sub>)<sub>2</sub>, complex [Ag<sub>2</sub>L<sub>2</sub><sup>2</sup>][ClO<sub>4</sub>]<sub>2</sub>: brown solid, yield 91%. m.p. 200–202 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, δ ppm): 8.07 (d, 2H), 7.98 (t, 2H), 7.82 (t, 2H), 7.48 (d, 2H), 7.37–7.07 (m, 10H), 6.84 (s, 2H), 6.51 (s, 2H), 3.76 (s, 2H), 3.50 (m, 2H), 1.69 (s, 6H), 1.22 (s, 12H). Anal. Calcd. for [Ag<sub>2</sub>L<sub>2</sub><sup>2</sup>][ClO<sub>4</sub>]<sub>2</sub> · 4CH<sub>3</sub>OH: C 61.83, H 5.26, N 6.14. Found: C 61.74, H 5.24, N 6.18%. IR (KBr, cm<sup>-1</sup>): 3750, 3482, 3061, 2961, 2926, 2868, 2011, 1772, 1618, 1588, 1469, 1439, 1362, 1317, 1252, 1095, 1007, 974, 924, 881, 798, 748, 701, 623.

Bis[4,4'-methylene-*N,N'*-(phenyl-2-pyridinylmethlene)-bis(2,6-diisopropyl-anil)] · (AgClO<sub>4</sub>)<sub>2</sub>, complex [Ag<sub>2</sub>L<sub>2</sub><sup>3</sup>][ClO<sub>4</sub>]<sub>2</sub>: pale yellow solid, yield 83%. m.p. >300 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, δ ppm): 8.64 (d, 2H), 8.01 (t, 2H), 7.86 (t, 2H), 7.51 (d, 2H), 7.35–7.29 (m, 10H), 6.89 (s, 2H), 6.36 (s, 2H), 3.65 (s, 2H), 3.26 (m, 2H), 2.55 (m, 2H), 1.61 (d, 6H), 1.29 (d, 12H), 0.73 (d, 6H). Anal. Calcd. for [Ag<sub>2</sub>L<sub>2</sub><sup>3</sup>][ClO<sub>4</sub>]<sub>2</sub> · 3CH<sub>3</sub>OH: C 63.64, H 6.09, N 5.88. Found: C 64.04, H 5.74, N 5.62%. IR (KBr, cm<sup>-1</sup>): 3453, 3059, 2962, 2871, 2011, 1618, 1463, 1441, 1383, 1360, 1316, 1253, 1212, 1095, 1005, 961, 852, 798, 747, 701, 625.

Bis[4,4'-methylene-*N,N'*-(phenyl-2-pyridinylmethlene)-bis(2,6-diethyl-anil)] · (AgClO<sub>4</sub>)<sub>2</sub>, complex [Ag<sub>2</sub>L<sub>2</sub><sup>4</sup>][ClO<sub>4</sub>]<sub>2</sub>: yellow solid, yield 91%. m.p. 247–248 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, δ ppm): 9.02 (m, 2H), 8.56 (m, 2H), 8.23 (d, 1H), 8.15–8.03 (m, 2H), 7.76 (d, 1H), 7.67 (t, 1H), 7.57–7.48 (m, 3H), 7.44–7.33 (m, 5H), 7.16 (m, 2H), 6.85 (d, 2H), 6.72 (d, 1H), 3.42 (s, 2H), 2.54 (m, 4H), 2.31 (m, 4H), 1.17–1.00 (m, 12H). Anal. Calcd. for [Ag<sub>2</sub>L<sub>2</sub><sup>4</sup>][ClO<sub>4</sub>]<sub>2</sub>: C 63.66, H 5.19, N 6.60. Found: C 63.63, H 5.18, N 6.18%. MALDI-FT-ICRMS: 747.26 [AgL<sup>4</sup>]<sup>+</sup>.

Table 1

Crystallographic data of the silver complex 2[Ag<sub>2</sub>L<sub>2</sub><sup>4</sup>][ClO<sub>4</sub>]<sub>2</sub> · 3CH<sub>3</sub>OH · 2C<sub>4</sub>H<sub>10</sub>O · CH<sub>3</sub>CN · H<sub>2</sub>O

Chemical formula:	Formula weight: 3696.08
C <sub>193</sub> H <sub>213</sub> Ag <sub>4</sub> Cl <sub>4</sub> N <sub>17</sub> O <sub>22</sub>	
<i>a</i> [Å] = 36.745(1)	Space group: <i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)
<i>b</i> [Å] = 19.421(1)	<i>T</i> [°C] = -75
<i>c</i> [Å] = 27.115(1)	<i>λ</i> = 0.71073 Å
<i>β</i> [°] = 111.19(1)	<i>ρ</i> <sub>calcd</sub> = 1.361 g cm <sup>-3</sup>
<i>V</i> [Å <sup>3</sup> ] = 18041.6(12)	<i>μ</i> (Mo Kα) = 5.58 cm <sup>-1</sup>
<i>Z</i> = 4	<i>R</i> = 0.0585 <sup>a</sup>
	<i>wR</i> = 0.1549 <sup>b</sup>

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

$$^b wR = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}. w = 1 / [\sigma^2(F_o^2) + (0.1048P)^2 + 4.6255P], P = (F_o^2 + 2F_c^2) / 3.$$

IR (KBr, cm<sup>-1</sup>): 3447, 3057, 2966, 2933, 2847, 2013, 1615, 1526, 1493, 1457, 1374, 1317, 1252, 1215, 1091, 1002, 968, 941, 882, 852, 792, 766, 743, 701, 663, 624.

### 2.4. X-ray crystal structure analyses

The crystals of silver complex [Ag<sub>2</sub>L<sub>2</sub><sup>4</sup>][ClO<sub>4</sub>]<sub>2</sub> suitable for X-ray diffraction were grown by the diffusion of diethyl ether to the CH<sub>3</sub>OH–CH<sub>3</sub>CN solution of complex. Data set was collected with a Nonius Kappa CCD diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN [15], absorption correction SORTAV [16], structure solution SHELXS-97 [17], structure refinement SHELXL-97 (G.M. Sheldrick, Universität Göttingen, 1997), graphics XP (Bruker-AXS, 1997). The crystal data and refinement parameters are summarized in Table 1. Goodness-of-fit for *F*<sup>2</sup> was 1.024. A total of 55,529 reflections were measured, 31,739 unique (*R*<sub>int</sub> = 0.037), *R* (for 19,284 reflections with *I* ≥ 2σ(*I*)) = 0.0585, *wR* = 0.1549. Largest diff. peak and hole 0.68 and -0.78 eÅ<sup>-3</sup>. Hydrogen atoms calculated and refined as riding atoms, water molecule has very close contact to the acetonitrile molecule.

## 3. Results and discussion

Ligand L was prepared by the condensation of two equivalent of benzoyl pyridine and one equivalent of 4,4'-methylene-bis(2,6-dialkylaniline). Reaction of L with silver(I) perchlorate in CH<sub>3</sub>OH–CH<sub>2</sub>Cl<sub>2</sub> yielded a pale red solution from which the title complex was obtained on treatment with diethyl ether. Besides the IR, <sup>1</sup>H NMR and elemental analysis evidences, mass spectrometry of [Ag<sub>2</sub>L<sub>2</sub><sup>4</sup>][ClO<sub>4</sub>]<sub>2</sub> displayed peaks corresponding to [AgL<sup>4</sup>]<sup>+</sup> consistent with the formation of metal ligand species.

The UV–vis spectra showed the characteristic absorption of ligands and complexes. The UV–vis spectra of all complexes ( $1 \times 10^{-4}$  mol/L in  $\text{CH}_2\text{Cl}_2$ ) showed the absorption maxima ( $\lambda_{\text{max}}$ ) around 405 nm with similar  $\epsilon$ . The  $\lambda_{\text{max}}$  (nm) values of complexes  $[\text{Ag}_2\text{L}_2^1][\text{ClO}_4]_2$ ,  $[\text{Ag}_2\text{L}_2^2][\text{ClO}_4]_2$ ,  $[\text{Ag}_2\text{L}_2^3][\text{ClO}_4]_2$ ,  $[\text{Ag}_2\text{L}_2^4][\text{ClO}_4]_2$  are 413, 410, 404 and 410, respectively, with corresponding  $\epsilon$  ( $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) values 4646, 4367, 4100 and 5168. The half-wave potentials ( $E_{1/2}$ ) (vs aqueous SCE, scan rate 100 mV/s) in polarogram of  $2 \times 10^{-3}$  mol/L dichloromethane solution with 0.1 mol/L  $(t\text{-Bu})_4\text{NClO}_4$  were also very similar:  $[\text{Ag}_2\text{L}_2^1][\text{ClO}_4]_2$ , 0.846;  $[\text{Ag}_2\text{L}_2^2][\text{ClO}_4]_2$ , 0.893;  $[\text{Ag}_2\text{L}_2^3][\text{ClO}_4]_2$ , 0.879 and  $[\text{Ag}_2\text{L}_2^4][\text{ClO}_4]_2$ , 0.865. The similar  $\lambda_{\text{max}}$ ,  $\epsilon$  and  $E_{1/2}$  data came from the similar coordination environment around Ag(I), where  $\text{Ag}^+$  cations with four sites of atoms [11]. In addition, their half-wave potential confirmed a similar oxidability or stability of these Ag(I) complexes in  $\text{CH}_2\text{Cl}_2$ . The IR absorption of imine ( $\text{C}=\text{N}$ ) in ligands  $\text{L}^1$ ,  $\text{L}^2$ ,  $\text{L}^3$  and  $\text{L}^4$  is 1632, 1629, 1627 and 1627  $\text{cm}^{-1}$ , respectively. After coordination with Ag(I), they correspondingly changed to 1620, 1618, 1618 and 1615  $\text{cm}^{-1}$ . Therefore, the other three complexes,  $[\text{Ag}_2\text{L}_2^i][\text{ClO}_4]_2$ ,

$[\text{Ag}_2\text{L}_2^2][\text{ClO}_4]_2$  and  $[\text{Ag}_2\text{L}_2^3][\text{ClO}_4]_2$ , are possibly own similar structure with  $[\text{Ag}_2\text{L}_2^4][\text{ClO}_4]_2$ .

In the crystal structure of complex  $[\text{Ag}_2\text{L}_2^4][\text{ClO}_4]_2$ , each asymmetric unit contains two  $[\text{Ag}_2\text{L}_2^4]^{2+}$  moieties (a and b). The molecular structure of two  $[\text{Ag}_2\text{L}_2^4]^{2+}$  moieties (a and b) in the asymmetric unit is showed in Fig. 1, while the hydrogen atoms, perchlorate anion and solvent molecules are omitted for clarity. The selected bond lengths and angles are listed in Table 2.

In two  $[\text{Ag}_2\text{L}_2^4]^{2+}$  moieties, each silver(I) cation was coordinated by four nitrogen atoms (from pyridylimine fragment), namely occupying a pseudo-tetrahedral environment bond to two pyridylimine fragments from two ligands. Therefore, two ligands coordinated two silver cations. In the dimeric  $[\text{Ag}_2\text{L}_2^4]^{2+}$  moiety (a) (containing Ag1 and Ag2), the normal direction of four phenylene ring planes of two ligands, plane 1 containing six carbon atoms (C25, C26, C27, C28, C29 and C30), plane 2 (from C36 to C41), plane 3 (from C125 to C130) and plane 4 (from C136 to C141), makes a angle of  $101.5^\circ$ ,  $95.3^\circ$ ,  $79.6^\circ$  and  $82.6^\circ$  with the Ag1–Ag2 axis, respectively. The plane 1 and plane 4 are on the opposite side with respect to the Ag1–Ag2 axis and are nearly

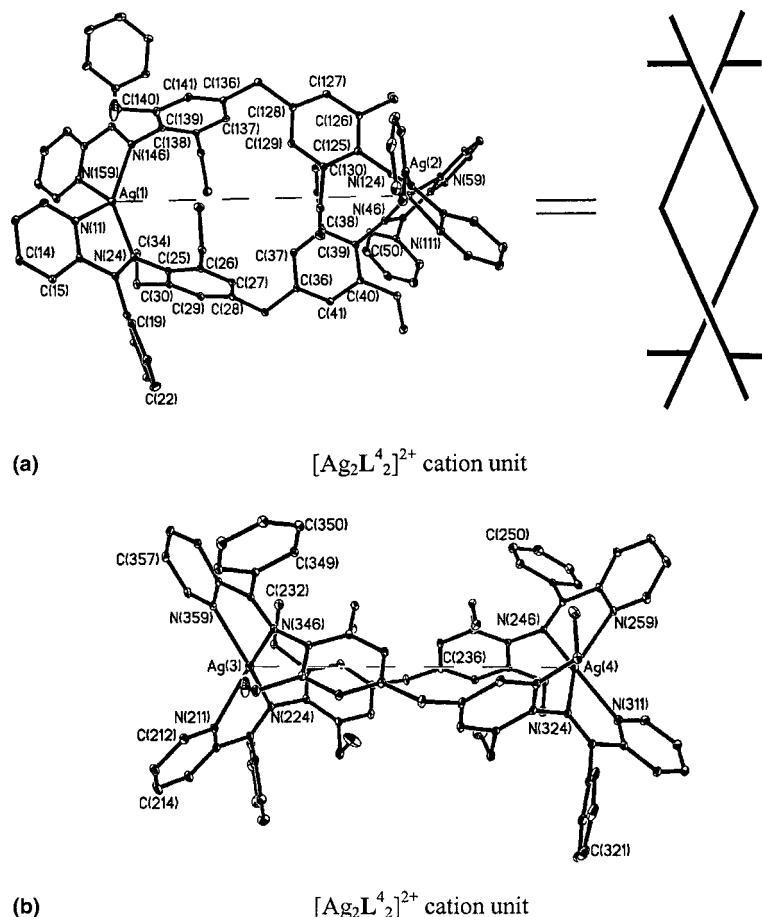


Fig. 1. Molecular structure of  $[\text{Ag}_2\text{L}_2^4]^{2+}$  cation units (a) and (b) in an asymmetric unit with thermal ellipsoids at 5% probability.

Table 2

Selected bond lengths and angles of the silver complex  $2[\text{Ag}_2\text{L}_2^4][\text{ClO}_4]_2 \cdot 3\text{CH}_3\text{OH} \cdot 2\text{C}_4\text{H}_{10}\text{O} \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ 

Bond lengths (Å)			
Ag(1)–N(24)	2.281(4)	Ag(1)–N(146)	2.301(4)
Ag(1)–N(159)	2.355(4)	Ag(1)–N(11)	2.356(4)
Ag(2)–N(124)	2.284(4)	Ag(2)–N(46)	2.291(4)
Ag(2)–N(111)	2.332(4)	Ag(2)–N(59)	2.333(4)
Ag(3)–N(346)	2.304(4)	Ag(3)–N(224)	2.304(4)
Ag(3)–N(359)	2.324(4)	Ag(3)–N(211)	2.347(4)
Ag(4)–N(324)	2.260(4)	Ag(4)–N(246)	2.290(4)
Ag(4)–N(259)	2.327(4)	Ag(4)–N(311)	2.355(5)
Angles (°)			
N(24)–Ag(1)–N(146)	140.92(14)	N(24)–Ag(1)–N(159)	138.55(14)
N(146)–Ag(1)–N(159)	70.58(15)	N(24)–Ag(1)–N(11)	71.35(14)
N(146)–Ag(1)–N(11)	128.02(14)	N(159)–Ag(1)–N(11)	113.91(15)
N(124)–Ag(2)–N(46)	141.84(14)	N(124)–Ag(2)–N(111)	71.97(14)
N(46)–Ag(2)–N(111)	122.31(14)	N(124)–Ag(2)–N(59)	138.41(14)
N(46)–Ag(2)–N(59)	71.34(14)	N(111)–Ag(2)–N(59)	116.21(15)
N(46)–C(47)–C(54)	117.7(4)	N(124)–C(117)–C(116)	117.4(4)
C(28)–C(35)–C(36)	114.7(4)	C(128)–C(135)–C(136)	114.8(4)
N(146)–C(147)–C(154)	116.6(5)	N(24)–C(17)–C(16)	117.4(5)
N(246)–C(247)–C(248)	125.1(4)	N(324)–C(317)–C(316)	118.6(5)
C(336)–C(335)–C(328)	114.8(4)	C(236)–C(235)–C(228)	114.9(4)
N(346)–C(347)–C(354)	116.5(4)	N(224)–C(217)–C(218)	125.4(5)

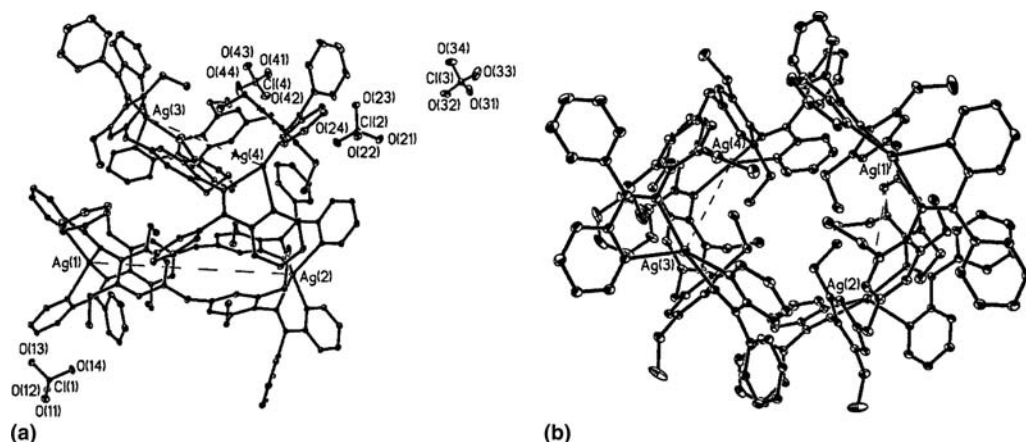


Fig. 2. The asymmetric unit (a) composed of two  $[\text{Ag}_2\text{L}_2^4]^{2+}$  cation units (along the *c*-axis) and the hole-like architecture (b) assembled by two  $[\text{Ag}_2\text{L}_2^4]$  moieties (along the *a*-axis).

parallel to each other with a dihedral angle of  $15.8^\circ$ , plane 2 and plane 3 are also on the opposite side with respect to the Ag1–Ag2 axis and make a dihedral angle of  $18.9^\circ$ , while two phenylene ring planes in the same ligand are nearly perpendicular to each other, such as plane 1 and plane 2 (included in a ligand) with a dihedral angle of  $80.1^\circ$  and plane 3 and plane 4 (included in another ligand) with a dihedral angle of  $82.6^\circ$ . So four phenylene ring planes wrap helically about the Ag1–Ag2 axis. The distance between Ag1 and Ag2 is 10.913 Å. The another dimeric  $[\text{Ag}_2\text{L}_2^4]^{2+}$  moiety (b) (containing Ag3 and Ag4) in the asymmetric unit is formed in very similar way with slightly varying the distances between Ag3 and Ag4 of 10.849 Å.

Looking carefully at the structure of the asymmetric unit (along the *c*-axis) (a in Fig. 2), it can be found that two independent dimeric  $[\text{Ag}_2\text{L}_2^4]^{2+}$  moieties were interacted together to compose an asymmetric unit and give rise to the double helical structure through weak bondings or other interactions (such as Van der waals interaction, hydrogen bonds and electrostatic interaction), while the perchlorate anions took parts in the pairing of two  $\text{Ag}_2\text{L}_2^4$  units (Tables 3 and 4). The Ag–Ag axis of two  $[\text{Ag}_2\text{L}_2^4]^{2+}$  moieties lies, respectively, on the diagonal lines of two opposite planes in a rectangular parallelepiped. The Ag1–Ag2 axis and the Ag3–Ag4 axis make an angle of  $52.6^\circ$ . The distance between Ag1 and Ag3, Ag2 and Ag4 is 8.651 and 8.671 Å, respectively.

Table 3

Intra- and inter-molecular contact (shorter than 3.6 Å) for silver complex  $2[\text{Ag}_2\text{L}_2^4][\text{ClO}_4]_2 \cdot 3\text{CH}_3\text{OH} \cdot 2\text{C}_4\text{H}_{10}\text{O} \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$

Contact	Distance (Å)
C34...C357	3.548
C36...C350	3.435
C50...C350	3.374
O14...C19	3.008
C150...C236	3.551
C215...O44 <sup>ii</sup>	3.353
C115...O21 <sup>iv</sup>	3.453
C52...C121 <sup>v</sup>	3.508
N359...O12 <sup>v</sup>	3.194
C213...O11 <sup>v</sup>	3.191
O12...C347 <sup>vi</sup>	3.443
C242...O23 <sup>vii</sup>	3.304
C252...C327 <sup>vii</sup>	3.450
C34...C232	3.480
C37...C349	3.567
O14...C20	3.088
C15...O13	3.325
C150...C250	3.515
C13...C219 <sup>iii</sup>	3.457
C114...O22 <sup>iv</sup>	3.242
C53...C121 <sup>v</sup>	3.554
C212...O11 <sup>v</sup>	3.142
C354...O12 <sup>v</sup>	3.140
C23...O44 <sup>vi</sup>	3.385
C252...C328 <sup>vii</sup>	3.585

(i)  $1-x, 0.5+y, 0.5-z$ ; (ii)  $1-x, 0.5+y, 1.5-z$ ; (iii)  $1-x, -0.5+y, 0.5-z$ ; (iv)  $-x, -0.5+y, 0.5-z$ ; (v)  $x, 0.5-y, 0.5+z$ ; (vi)  $x, 0.5-y, -0.5+z$ ; (vii)  $x, 1.5-y, 0.5+z$ .

Table 4

Intra- and inter-molecular hydrogen bonds geometry for silver complex  $2[\text{Ag}_2\text{L}_2^4][\text{ClO}_4]_2 \cdot 3\text{CH}_3\text{OH} \cdot 2\text{C}_4\text{H}_{10}\text{O} \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$

X-H...Y	Distance (Å)	Angle (°)
C14-H14...O13	3.174	129.9
C55-H55...O24	3.389	152.1
C232-H23D...O13 <sup>i</sup>	3.429	143.9
C357-H357...O12 <sup>i</sup>	3.454	143.7
C214-H214...O44 <sup>ii</sup>	3.015	125.4
C22-H22...O44 <sup>iv</sup>	3.167	131.6
C212-H212...O12 <sup>v</sup>	3.300	130.2
C355-H355...O42 <sup>vi</sup>	3.446	125.7
C321-H321...O34 <sup>iii</sup>	3.435	153.8
C15-H15...O14	3.423	132.9
C56-H56...O22	3.467	138.8
C157-H157...O13 <sup>i</sup>	3.461	143.5
C358-H358...O13 <sup>i</sup>	3.432	128.8
C215-H215...O43 <sup>iii</sup>	3.283	137.3
C114-H114...O21 <sup>iv</sup>	3.335	120.8
C29-H29...O42 <sup>vi</sup>	3.425	121.3
C312-H312...O23 <sup>vii</sup>	3.467	171.4

(i)  $1-x, 0.5+y, 0.5-z$ ; (ii)  $1-x, 0.5+y, 1.5-z$ ; (iii)  $1-x, -0.5+y, 0.5-z$ ; (iv)  $-x, -0.5+y, 0.5-z$ ; (v)  $x, 0.5-y, 0.5+z$ ; (vi)  $x, 0.5-y, -0.5+z$ ; (vii)  $x, 1.5-y, 0.5+z$ .

The shortest Van der Waals contact is C50...C350 with a distance of 3.374 Å. The shortest electrostatic interaction is O22...Ag2 with a distance of 8.180 Å.

In the each asymmetric unit composed by two independent  $[\text{Ag}_2\text{L}_2^4]^{2+}$  moieties, the twisting of the

$[\text{Ag}_2\text{L}_2^4]^{2+}$  cations resulted in a distorted cavity at the center of the asymmetric unit, thus giving a 'hole' with the potential to trap small molecules while being viewed along the *a*-axis (b in Fig. 2).

In addition to the intramolecular hydrogen bonds, perchlorate anions also made contributions for their intermolecular hydrogen bonds. Therefore, the silver complexes, consisting of discrete monomers of asymmetric unit (dual  $[\text{Ag}_2\text{L}_2^4]^{2+}$  moieties), formed a more sophisticated aggregates through hydrogen bonds to link neighboring asymmetric units as the infinite double helix (Fig. 3).

In summary, we obtained four Ag(I) complexes with sterically hindered bridged ligand 4,4'-methylene-*N,N'*-bis(phenyl-2-pyridylmethylene)-bis(2,6-dialkylanil)s and found the formation of the basic supramolecular unit and its aggregation into a complicated helical array through weak bonding and hydrogen bonds for complex  $[\text{Ag}_2\text{L}_2^4][\text{ClO}_4]_2$ . Although this assembly was formed in the solid state, the detail structures information of complexes in solution is not very clear. That does not

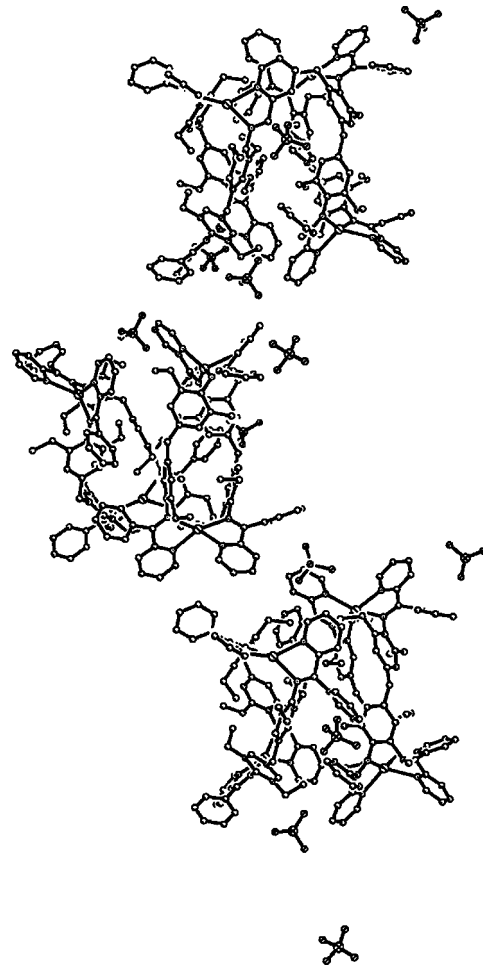


Fig. 3. Side view of the double helical aggregate (solvent molecules and all hydrogen atoms have been omitted for clarity).

provide a barrier to its application, since the weak non-covalent interactions are capable of achieving order at surfaces and interfaces. This metal/ligand couples and their binding small molecules provided the model to investigate helical supramolecular aggregation and their cavity formed by the dimeric moieties.

#### 4. Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as CCDC-191026. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

#### Acknowledgements

We thank the National Natural Science Foundation of China for financial support under Grant No. 20272062. W.H.S. thanks Prof. Dr. Gerhard Erker in Institute of Organic Chemistry of Münster University and Alexander von Humboldt-Stiftung.

#### References

- [1] J.-M. Lehn, in: *Comprehensive Supramolecular Chemistry*, vol. 9, Pergamon, Oxford, 1996.
- [2] M. Fujita, *Acc. Chem. Res.* 32 (1999) 53.
- [3] S. Leininger, B. Olenyuk, P.J. Stang, *Chem. Rev.* 100 (2000) 853.
- [4] D.L. Caulder, K.N. Raymond, *Acc. Chem. Res.* 32 (1999) 975.
- [5] C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* 97 (1997) 2005.
- [6] M. Albrecht, *Chem. Rev.* 101 (2001) 3457.
- [7] N. Yoshida, H. Oshio, T. Ito, *J. Chem. Soc., Perkin Trans. 2* (1999) 975.
- [8] N. Yoshida, H. Oshio, T. Ito, *J. Chem. Soc., Perkin Trans. 2* (2001) 1674.
- [9] P.E. Kruger, N. Martin, M. Nieuwenhuyzen, *J. Chem. Soc., Dalton Trans.* (2001) 1966.
- [10] M.J. Hannon, C.L. Painting, A. Jackson, J. Hamblin, W. Errington, *Chem. Commun.* (1997) 1807.
- [11] M.J. Hannon, S. Bunce, A.J. Clarke, N.W. Alcock, *Angew. Chem. Int. Ed.* 38 (1999) 1277.
- [12] L.J. Childs, N.W. Alcock, M.J. Hannon, *Angew. Chem. Int. Ed.* 40 (2001) 1079.
- [13] A. Luetzen, M. Hapke, J. Griep-Raming, D. Haase, W. Saak, *Angew. Chem. Int. Ed.* 41 (2002) 2086.
- [14] B.E. Love, J.H. Ren, *J. Org. Chem.* 58 (1993) 5556.
- [15] Z. Otwinowski, W. Minor, *Methods Enzymol.* 276 (1997) 307.
- [16] (a) R.H. Blessing, *Acta Cryst. A* 51 (1995) 33;  
(b) R.H. Blessing, *J. Appl. Cryst.* 30 (1997) 421.
- [17] G.M. Sheldrick, *Acta Cryst. A* 46 (1990) 467.