

## Synthesis and X-ray structures of new chiral Ag(I) complexes with biaryl-based N<sub>4</sub>-donor ligands

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### Abstract

Condensation of (*R*)-2,2'-diamino-1,1'-binaphthyl or (*R*)-6,6'-dimethylbiphenyl-2,2'-diamine with 2 equiv of 2-pyridine carboxaldehyde in toluene in the presence of molecular sieves at 70 °C gives (*R*)-*N,N'*-bis(pyridin-2-ylmethylene)-1,1'-binaphthyl-2,2'-diimine (**1**), and (*R*)-*N,N'*-bis(pyridin-2-ylmethylene)-6,6'-dimethylbiphenyl-2,2'-diimine (**3**), respectively, in good yields. Reduction of **1** with an excess of NaBH<sub>4</sub> in a solvent mixture of MeOH and toluene (1:1) at 50 °C gives (*R*)-*N,N'*-bis(pyridin-2-ylmethyl)-1,1'-binaphthyl-2,2'-diamine (**2**) in 95% yield. Rigidity plays an important role in the formation of helicate silver(I) complexes. Treatment of **1**, or **3** with 1 equiv of AgNO<sub>3</sub> in mixed solvents of MeOH and CH<sub>2</sub>Cl<sub>2</sub> (1:4) gives the chiral, dinuclear double helicate Ag(I) complexes [Ag<sub>2</sub>(**1**)<sub>2</sub>][NO<sub>3</sub>]<sub>2</sub> (**4**) and [Ag<sub>2</sub>(**3**)<sub>2</sub>][NO<sub>3</sub>]<sub>2</sub> · 2H<sub>2</sub>O (**6**), respectively, in good yields. While under the similar reaction conditions, reaction of **2** with 1 equiv of AgNO<sub>3</sub> affords the chiral, mononuclear single helicate Ag(I) complex [Ag(**2**)][NO<sub>3</sub>] (**5**) in 90% yield. [Ag<sub>2</sub>(**1**)<sub>2</sub>][NO<sub>3</sub>]<sub>2</sub> (**4**) can further react with excess AgNO<sub>3</sub> to give [Ag<sub>2</sub>(**1**)<sub>2</sub>]<sub>3</sub>[NO<sub>3</sub>]<sub>2</sub>[Ag(CH<sub>3</sub>OH)(NO<sub>3</sub>)<sub>3</sub>]<sub>2</sub> · 2CH<sub>3</sub>OH (**7**) in 75% yield. All compounds have been fully characterized by various spectroscopic techniques and elemental analyses. Compounds **1** and **5–7** have been further subjected to single-crystal X-ray diffraction analyses.

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**Keywords:** Ag(I) complexes; Synthesis; Crystal structure; Helix

### 1. Introduction

In recent years, chiral Ag(I) complexes have been designed and prepared to give variants which bear appropriate structural and electronic features for intended specific reactions [1–17], and these complexes have been shown to exhibit good to excellent enantioselectivities in a number of asymmetric reactions such as cycloaddition reactions [1–3], Heck reactions [4,5], Michael addition reactions [6], Mannich reactions [7,8], and other transformations [9–17].

Although many chiral silver(I) complex catalysts have been known, the development of new chiral silver(I) complex is desirable. Previously, we reported the chiral ligand (*R*)-*N,N'*-bis(pyridin-2-ylmethylene)-1,1'-binaphthyl-2,2'-diimine (**1**), and it has been shown that its Ir(I), Rh(I), and Ti(IV) complexes are useful catalysts for a range of asymmetric transformations [18,19]. In our attempt to further explore the coordination chemistry of ligand **1**, we recently extended our research work to Ag(I) chemistry. For better understanding and comparison, we also included the ligands (*R*)-*N,N'*-bis(pyridin-2-ylmethyl)-1,1'-binaphthyl-2,2'-diamine (**2**) and (*R*)-*N,N'*-bis(pyridin-2-ylmethylene)-6,6'-dimethylbiphenyl-2,2'-diimine (**3**) in our research effort. Herein we report a detailed study on the synthesis, structural characterization of Ag(I) complexes with ligands **1–3**.

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## 2. Experimental

### 2.1. General methods

All chemicals were purchased from Aldrich Chemical Co. and Beijing Chemical Co. used as received unless otherwise noted. (*R*)-2,2'-Diamino-1,1'-binaphthyl [20,21], and (*R*)-6,6'-dimethylbiphenyl-2,2'-diamine [22] were prepared according to the literature methods. Infrared spectra were obtained from KBr pellets on an Avatar 360 Fourier transform spectrometer.  $^1\text{H}$  NMR spectra were recorded on a Bruker AV-500 spectrometer. All chemical shifts are reported in  $\delta$  units with reference to the residual protons of the deuterated solvents. Melting points were measured on an X-6 melting point apparatus (Beijing Tech. Instrument Co. Ltd.) and were uncorrected. Elemental analyses were performed on a Vario EL elemental analyzer by the analytical laboratory, Beijing Normal University, Beijing, China.

### 2.2. Preparation of (*R*)-*N,N'*-bis(pyridin-2-ylmethylene)-1,1'-binaphthyl-2,2'-diimine (**1**)

This compound was prepared according to a modified literature procedure [18,19]. Pyridine-2-carboxaldehyde (2.14 g, 20.0 mmol) was mixed with (*R*)-2,2'-diamino-1,1'-binaphthyl (2.84 g, 10.0 mmol) in dry toluene (50 mL). A few 4 Å molecular sieves were added, and the solution was warmed up to 70 °C and kept for one day at this temperature. The solution was filtered and the solvent was removed under reduced pressure. The resulting yellow solid was recrystallized from mixed solvents (20 mL) of benzene and *n*-hexane (1:1) to give **1** as yellow crystals. Yield: 4.39 g (95%). M.p.: 147–149 °C.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  8.77 (s, 2H), 8.26 (d,  $J = 4.5$  Hz, 2H), 7.70–7.63 (m, 6H), 7.53 (d,  $J = 8.4$  Hz, 2H), 7.22–7.11 (m, 6H), 7.00 (t,  $J = 7.8$  Hz, 2H), 6.69 (t,  $J = 7.5$  Hz, 2H), 6.40 (t,  $J = 5.4$  Hz, 2H). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  3053 (w), 3003 (w), 1627 (s), 1613 (s), 1588 (s), 1567 (s), 1471 (s), 1330 (s), 1204 (s), 973 (s), 819 (vs), 776 (vs), 753 (vs), 745 (vs). Anal. Calc. for  $\text{C}_{32}\text{H}_{22}\text{N}_4$ : C, 83.1; H, 4.79; N, 12.1. Found: C, 83.1; H, 5.13; N, 11.8.

### 2.3. Preparation of (*R*)-*N,N'*-bis(pyridin-2-ylmethyl)-1,1'-binaphthyl-2,2'-diamine (**2**)

(*R*)-*N,N'*-Bis(pyridin-2-ylmethylene)-1,1'-binaphthyl-2,2'-diimine (**1**) (2.31 g, 5.0 mmol) was dissolved in a mixed solvent (40 mL) of toluene and methanol (1:1),  $\text{NaBH}_4$  (2.00 g, 52.6 mmol) was added in small portions at 0 °C, then the solution was warmed up to 50 °C and kept for 2 h at this temperature. The solvent was removed and the residue was decomposed with  $\text{H}_2\text{O}$  (20 mL) and extracted with ethyl acetate (20 mL  $\times$  3) and washed with brine (20 mL). The combined organic layers were dried with anhydrous  $\text{Na}_2\text{SO}_4$  and the solvent was removed under reduced pressure to give a white solid **2**. Yield: 2.21 g

(95%). M.p.: 150–152 °C.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  8.31 (d,  $J = 4.8$  Hz, 2H), 7.68–7.65 (m, 4H), 7.36–7.32 (m, 2H), 7.16–7.04 (m, 6H), 6.97 (d,  $J = 3.6$  Hz, 4H), 6.56–6.51 (m, 2H), 4.69 (t,  $J = 6.3$  Hz, 2H,  $\text{CH}_2$ ), 4.21–4.06 (m, 4H,  $\text{CH}_2$  and  $\text{NH}$  overlap). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  3407 (m), 3301 (m), 3051 (m), 3007 (w), 2909 (w), 1615 (vs), 1592 (vs), 1568 (s), 1508 (vs), 1489 (vs), 1423 (vs), 1335 (vs), 1304 (s), 1151 (s), 809 (vs), 748 (vs). Anal. Calc. for  $\text{C}_{32}\text{H}_{26}\text{N}_4$ : C, 82.4; H, 5.62; N, 12.0. Found: C, 82.2; H, 5.82; N, 11.8.

### 2.4. Preparation of (*R*)-*N,N'*-bis(pyridin-2-ylmethylene)-6,6'-dimethylbiphenyl-2,2'-diimine (**3**)

Pyridine-2-carboxaldehyde (1.07 g, 10.0 mmol) was mixed with (*R*)-6,6'-dimethylbiphenyl-2,2'-diamine (1.06 g, 5.0 mmol) in dry toluene (25 mL). A few 4 Å molecular sieves were added, and the solution was warmed up to 70 °C and kept for one day at this temperature. The solution was filtered and the solvent was removed under reduced pressure. The resulting yellow oil was washed with *n*-hexane (10 mL  $\times$  3) and dried under reduced pressure to give a light yellow oil **3**. Yield: 1.46 g (75%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.59 (d,  $J = 4.3$  Hz, 2H), 8.41 (s, 2H), 7.69 (d,  $J = 7.7$  Hz, 2H), 7.64 (t,  $J = 7.4$  Hz, 2H), 7.31–7.26 (m, 4H), 7.16 (d,  $J = 7.4$  Hz, 2H), 6.96 (d,  $J = 7.7$  Hz, 2H), 2.08 (s, 6H). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  3055 (s), 3009 (s), 2954 (s), 2918 (s), 2868 (m), 1632 (vs), 1585 (vs), 1567 (vs), 1468 (vs), 1435 (vs), 1243 (m), 1220 (s), 1042 (s), 992 (s), 789 (vs), 746 (vs). Anal. Calc. for  $\text{C}_{26}\text{H}_{22}\text{N}_4$ : C, 80.0; H, 5.68; N, 14.4. Found: C, 79.7; H, 6.05; N, 14.2.

### 2.5. Preparation of [ $\text{Ag}_2(\mathbf{1})_2$ ][ $\text{NO}_3$ ]<sub>2</sub> (**4**)

A  $\text{CH}_2\text{Cl}_2$  solution (20 mL) of **1** (0.46 g, 1.0 mmol) was added to a methanol solution (5 mL) of  $\text{AgNO}_3$  (0.17 g, 1.0 mmol) with stirring at room temperature. The solution was stirred for 5 h at room temperature and filtered. The solution was reduced to 3 mL and cooled to –20 °C, yielding pale yellow microcrystals, which were isolated by filtration. Yield: 0.60 g (95%). M.p.: 327–329 °C (dec.).  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ ):  $\delta$  8.95 (d,  $J = 9.0$  Hz, 2H), 8.20 (m, 2H), 8.04 (d,  $J = 7.7$  Hz, 2H), 7.58 (d,  $J = 8.1$  Hz, 2H), 7.50 (d,  $J = 8.8$  Hz, 2H), 7.48 (m, 2H), 7.35 (t,  $J = 7.1$  Hz, 2H), 7.19 (t,  $J = 7.5$  Hz, 2H), 7.12 (d,  $J = 8.8$  Hz, 2H), 6.82 (d,  $J = 8.6$  Hz, 2H), 6.78 (d,  $J = 4.2$  Hz, 2H). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  3044 (w), 3000 (w), 2963 (w), 1622 (w), 1585 (w), 1384 (s), 1297 (w), 1150 (w), 1043 (w), 898 (w), 821 (w), 750 (w). Anal. Calc. for  $\text{C}_{64}\text{H}_{44}\text{N}_{10}\text{Ag}_2\text{O}_6$ : C, 60.8; H, 3.51; N, 11.1. Found: C, 60.5; H, 3.82; N, 10.8.

### 2.6. Preparation of [ $\text{Ag}(\mathbf{2})$ ][ $\text{NO}_3$ ] (**5**)

This compound was prepared as colorless crystals from the reaction of **2** (0.47 g, 1.0 mmol) and  $\text{AgNO}_3$  (0.17 g, 1.0 mmol) in a mixed solvent (25 mL) of methanol and

CH<sub>2</sub>Cl<sub>2</sub> (1:4) by procedures similar to those used in the synthesis of **4**. Yield: 0.57 g (90%). M.p.: 218–220 °C (dec.). <sup>1</sup>H NMR (CD<sub>3</sub>OD/CDCl<sub>3</sub>; 1:4): δ 8.60 (d, *J* = 4.1 Hz, 2H), 8.01 (t, *J* = 7.6 Hz, 2H), 7.83 (t, *J* = 9.3 Hz, 4H), 7.63 (d, *J* = 7.7 Hz, 2H), 7.48 (t, *J* = 6.2 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 7.0 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 4.50 (d, *J* = 16.6 Hz, 2H), 4.46 (d, *J* = 16.6 Hz, 2H); protons of NH were not observed. IR (KBr, cm<sup>-1</sup>): ν 3385 (w), 3052 (w), 2896 (w), 1615 (s), 1596 (s), 1508 (s), 1491 (s), 1436 (s), 1383 (s), 1362 (vs), 1338 (vs), 1286 (s), 825 (s), 809 (s). Anal. Calc. for C<sub>32</sub>H<sub>26</sub>N<sub>5</sub>AgO<sub>3</sub>: C, 60.4; H, 4.12; N, 11.0. Found: C, 60.0; H, 4.33; N, 10.9.

### 2.7. Preparation of [Ag<sub>2</sub>(**3**)<sub>2</sub>][NO<sub>3</sub>]<sub>2</sub> · 2H<sub>2</sub>O (**6**)

This compound was prepared as pale yellow crystals from the reaction of **3** (0.39 g, 1.0 mmol) and AgNO<sub>3</sub> (0.17 g, 1.0 mmol) in mixed solvents (25 mL) of methanol and CH<sub>2</sub>Cl<sub>2</sub> (1:4) by procedures similar to those used in the synthesis of **4**. Yield: 0.54 g (93%). M.p.: 308–310 °C (dec.). <sup>1</sup>H NMR (CD<sub>3</sub>OD): δ 8.78 (d, *J* = 9.0 Hz, 2H), 8.20 (m, 2H), 8.05 (d, *J* = 7.7 Hz, 2H), 7.83 (d, *J* = 4.2 Hz, 2H), 7.65 (m, 2H), 6.97 (m, 4H), 6.36 (t, *J* = 7.8 Hz, 2H), 1.65 (s, 6H); protons of H<sub>2</sub>O were overlapped with H<sub>2</sub>O in CD<sub>3</sub>OD. IR (KBr, cm<sup>-1</sup>): ν 3457 (br, s), 3051 (w), 2918 (w), 2844 (w), 1624 (w), 1587 (m), 1453 (w), 1384 (vs), 1355 (s), 1304 (m), 1209 (w), 1150 (w), 1002 (w), 795 (m), 740 (m). Anal. Calc. for C<sub>52</sub>H<sub>48</sub>N<sub>10</sub>Ag<sub>2</sub>O<sub>8</sub>: C, 54.0; H, 4.18; N, 12.1. Found: C, 53.7; H, 4.25; N, 12.0.

### 2.8. Preparation of [Ag<sub>2</sub>(**1**)<sub>2</sub>]<sub>3</sub>[NO<sub>3</sub>]<sub>2</sub>[Ag(CH<sub>3</sub>OH)(NO<sub>3</sub>)<sub>3</sub>]<sub>2</sub> · 2CH<sub>3</sub>OH (**7**)

AgNO<sub>3</sub> (34 mg, 0.2 mmol) was added to a methanol solution (5 mL) of **4** (126 mg, 0.1 mmol) with stirring at room temperature. The solution was stirred for 2 h at room temperature and filtered. The solution was reduced to 1 mL and cooled to -20 °C, yielding pale yellow crystals, which were isolated by filtration. Yield: 107 mg (75%). M.p.: 328–330 °C (dec.). <sup>1</sup>H NMR (CD<sub>3</sub>OD): δ 8.95 (d, *J* = 9.0 Hz, 2H), 8.20 (m, 2H), 8.04 (d, *J* = 7.7 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.48 (m, 2H), 7.35 (t, *J* = 7.1 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 4.2 Hz, 2H), 3.37 (s, 2H, CH<sub>3</sub>OH); protons of CH<sub>3</sub>OH were not observed. IR (KBr, cm<sup>-1</sup>): ν 3442 (br, s), 3044 (w), 2911 (w), 2844(w), 1623 (w), 1585 (m), 1502 (w), 1384 (vs), 1297 (w), 1264 (w), 1202 (w), 1153 (w), 1094 (w), 1005 (w), 823 (m), 776 (m), 751 (m). Anal. Calc. for C<sub>196</sub>H<sub>148</sub>N<sub>32</sub>Ag<sub>8</sub>O<sub>28</sub>: C, 55.2; H, 3.50; N, 10.5. Found: C, 55.5; H, 3.82; N, 10.5.

### 2.9. X-ray crystallography

Single-crystal X-ray diffraction measurements were carried out on a Bruker SMART CCD diffractometer at 294(2) K using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction was applied using the SADABS program [23]. All structures were solved by direct methods and refined by full-matrix least squares on *F*<sup>2</sup> using the SHELXL-97 program package [24].

Table 1  
Crystal data and experimental parameters for compounds **1** and **5–7**

Compound	<b>1</b>	<b>5</b>	<b>6</b>	<b>7</b>
Formula	C <sub>32</sub> H <sub>22</sub> N <sub>4</sub>	C <sub>32</sub> H <sub>26</sub> N <sub>5</sub> AgO <sub>3</sub>	C <sub>52</sub> H <sub>48</sub> N <sub>10</sub> Ag <sub>2</sub> O <sub>8</sub>	C <sub>98</sub> H <sub>74</sub> N <sub>16</sub> Ag <sub>4</sub> O <sub>14</sub>
Formula weight	462.54	636.45	1156.74	2131.21
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> 2(1)	<i>P</i> 2(1)	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub>	<i>C</i> 12 <sub>1</sub>
<i>a</i> (Å)	8.140(2)	9.957(2)	14.700(5)	28.845(4)
<i>b</i> (Å)	10.962(3)	9.458(2)	16.862(5)	22.241(3)
<i>c</i> (Å)	13.953(4)	14.522(2)	19.576(6)	13.963(2)
β (°)	90.654(5)	99.333(5)	90	94.973(4)
<i>V</i> (Å <sup>3</sup> )	1245.1(6)	1349.4(3)	4852(3)	8924(2)
<i>Z</i>	2	2	4	4
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.234	1.566	1.578	1.586
μ(Mo Kα) <sub>calc</sub> (mm <sup>-1</sup> )	0.074	0.791	0.874	0.940
Size (mm)	0.38 × 0.22 × 0.20	0.28 × 0.26 × 0.20	0.22 × 0.18 × 0.16	0.12 × 0.10 × 0.02
<i>F</i> (000)	484	648	2336	4296
2θ Range (°)	2.92–52.86	2.84–53.04	3.08–55.80	3.66–50.00
Number of reflections collected	6959	7802	61 889	34 090
Number of unique reflections	4681 ( <i>R</i> <sub>int</sub> = 0.039)	4688 ( <i>R</i> <sub>int</sub> = 0.019)	11 601 ( <i>R</i> <sub>int</sub> = 0.050)	14 407 ( <i>R</i> <sub>int</sub> = 0.084)
Number of observed reflections	4681	4688	11 601	14 407
Number of variables	325	378	691	1208
Absorption correction ( <i>T</i> <sub>max</sub> , <i>T</i> <sub>min</sub> )	1.00, 0.77	0.86, 0.81	0.87, 0.83	0.98, 0.90
<i>R</i>	0.048	0.025	0.043	0.079
<i>R</i> <sub>w</sub>	0.089	0.063	0.096	0.187
<i>R</i> <sub>all</sub>	0.114	0.028	0.047	0.091
Goodness-of-fit	1.01	1.08	1.06	1.06

Table 2  
Selected bond distances (Å) and bond angles (°) for **1** and **5–7**

Compound	Torsions			Ag–N (av)	Others
	Aryl–imine	Pyridyl–imine	Aryl–aryl		
<b>1</b>	38.0(3)	4.8(3)	70.2(3)		C=N (av)
	53.7(3)	23.0(3)			1.263(4)
<b>5</b>			82.6(3)	2.457(2)	
<b>6</b>	0.1(4)	42.9(4)	73.8(4)	2.359(3)	C=N (av)
	0.4(4)	45.2(4)	73.9(4)		1.275(5)
	4.7(4)	46.5(4)			Ag···Ag
	7.0(4)	52.9(4)			3.687(5)
	2.1(8)	34.1(8)	68.6(8)	2.333(10)	C=N (av)
<b>7</b>	3.6(8)	36.7(8)	73.2(8)		1.289(15)
	6.4(8)	39.6(8)			Ag···Ag
	9.7(8)	44.6(8)			3.760(15)

Most of the hydrogen atoms (excluding those of the solvated  $H_2O$  and  $CH_3OH$ ) were geometrically fixed using the riding model. The crystal data and experimental data for **1**, **5–7** are summarized in Table 1. Selected bond lengths and torsion angles are listed in Table 2.

### 3. Results and discussion

#### 3.1. Synthesis and characterization of ligands **1–3**

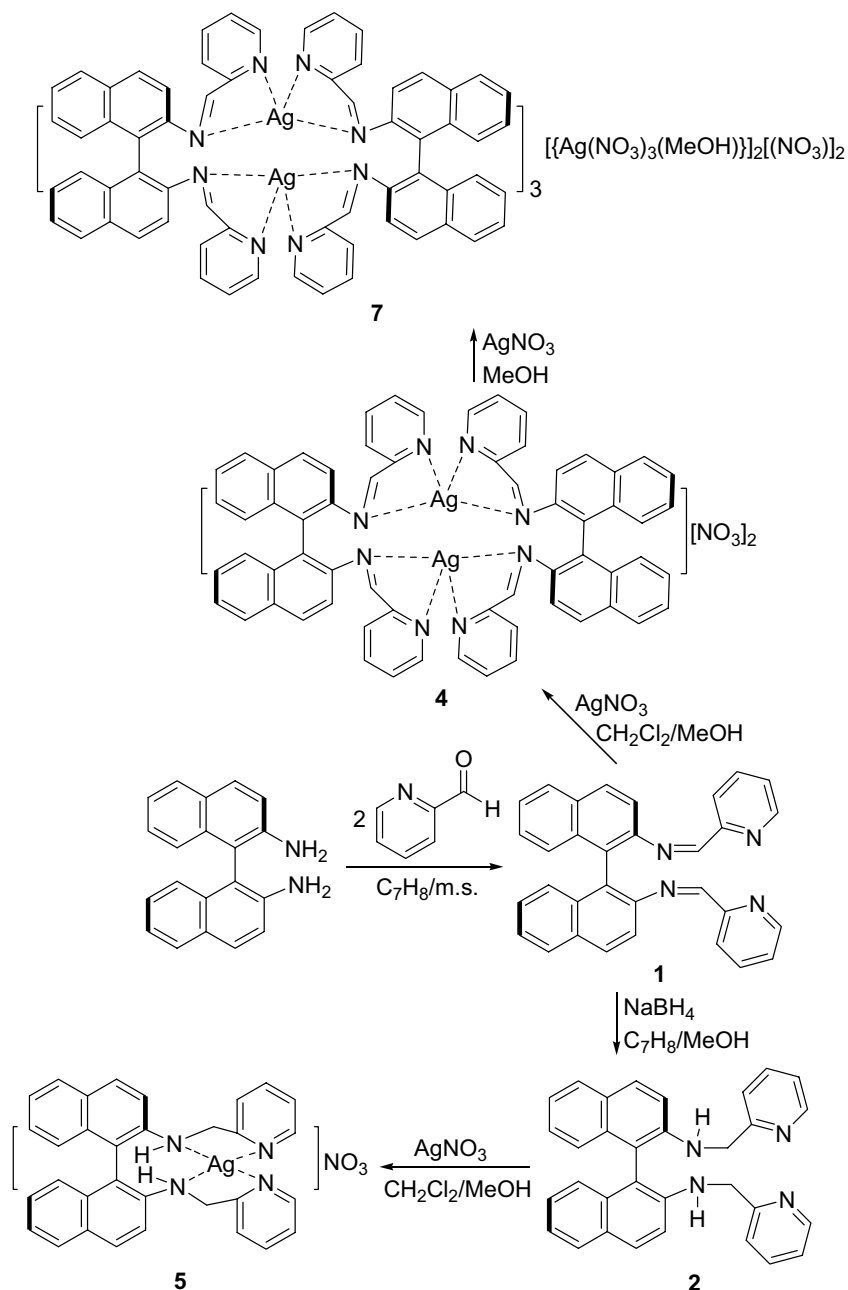
Condensation of (*R*)-2,2'-diamino-1,1'-binaphthyl or (*R*)-6,6'-dimethylbiphenyl-2,2'-diamine with 2 equiv of 2-pyridine carboxaldehyde in toluene in the presence of molecular sieves at 70 °C gives (*R*)-*N,N'*-bis(pyridin-2-ylmethylene)-1,1'-binaphthyl-2,2'-diimine (**1**), and (*R*)-*N,N'*-bis(pyridin-2-ylmethylene)-6,6'-dimethylbiphenyl-2,2'-diimine (**3**), respectively, in good yields (Schemes 1 and 2). Reduction of **1** with an excess of  $NaBH_4$  in a solvent mixture of MeOH and toluene (1:1) at 50 °C gives (*R*)-*N,N'*-bis(pyridin-2-ylmethyl)-1,1'-binaphthyl-2,2'-diamine (**2**) in 95% yield (Scheme 1). Compounds **1–3** are air-stable and very soluble in  $CH_2Cl_2$ ,  $CHCl_3$ , toluene, and benzene, and only slightly soluble in *n*-hexane. Ligands **1–3** have been fully characterized by various spectroscopic techniques and elemental analyses. The  $^1H$  NMR spectra of **1–3** indicate that they are symmetrical on the NMR timescale. The IR spectra of **1** and **3** show a typical characteristic N=C absorption at about  $1630\text{ cm}^{-1}$ , and this absorption disappears upon treatment of **1** with excess  $NaBH_4$ , supporting the formation of **2**. The solid-state structure of **1** has been confirmed by single-crystal X-ray diffraction analyses.

The molecular structure of **1** shows that it crystallizes in a  $C_2$  symmetric distorted-tetrahedral geometry (Fig. 1). As expected, the average distance (1.263(4) Å) of C=N is in agreement with a C=N double bond. The naphthalene units are twisted with respect to the imine group (torsion angles are  $38.0(3)^\circ$  and  $53.7(3)^\circ$ ), and a more dramatic twisting is observed between the naphthalene rings which are almost perpendicular to each other (torsion angle is  $70.2(3)^\circ$ ), which is larger than that ( $63.9(6)^\circ$ ) found in (*R*)-2,2'-diamino-1,1'-binaphthyl [25].

#### 3.2. Synthesis and characterization of complexes **4–7**

Treatment of **1**, **2**, or **3** with 1 equiv of  $AgNO_3$  in mixed solvents of MeOH and  $CH_2Cl_2$  (1:4) gives the chiral, ionic Ag(I) complexes  $[Ag_2(\mathbf{1})_2][NO_3]_2$  (**4**),  $[Ag(\mathbf{2})][NO_3]$  (**5**), and  $[Ag_2(\mathbf{3})_2][NO_3]_2 \cdot 2H_2O$  (**6**), respectively, in good yields (Schemes 1 and 2).  $[Ag_2(\mathbf{1})_2][NO_3]_2$  (**4**) can further react with excess  $AgNO_3$  to give  $[Ag_2(\mathbf{1})_2]_3[NO_3]_2[Ag(CH_3OH)(NO_3)_3]_2 \cdot 2CH_3OH$  (**7**) in 75% yield (Scheme 1). Complexes **4–7** are air-stable and soluble in methanol, partially soluble in  $CH_2Cl_2$ ,  $CHCl_3$ , and acetone, and insoluble in *n*-hexane, toluene, and benzene. They have been fully characterized by various spectroscopic techniques and elemental analyses. The  $^1H$  NMR chemical shifts data and coupling constants for compounds **4** and **7** in  $CD_3OD$  solution are identical. This is consistent with formation of the same cation in compounds **4** and **7**. The spectra of **4**, **5**, **6**, and **7** indicate that the complexes are symmetrical on the NMR timescale. The imine resonances display doublet splitting with distinctive coupling to the silver(I) ion of  $^3J_{Ag-H} = 9.0\text{ Hz}$  at 8.95 ppm for **4** and **7**, and at 8.78 ppm for **6**, which confirms coordination to the metal. These spectroscopic data are very close to those found in  $[Ag_2(C_{32}H_{22}N_4)_2][PF_6]_2$ , and the cations retain in dinuclear formulation in solution [26]. The infrared spectra of these salts exhibit peaks corresponding to aromatic stretches in addition to weak imine stretches at  $1623\text{ cm}^{-1}$  for **4**, **6**, and **7**, and N–H stretches at  $3385\text{ cm}^{-1}$  for **5**. The solid-state structures of complexes **5**, **6**, and **7** have been further confirmed by single-crystal X-ray diffraction analyses.

The single-crystal structure of complex **5** shows that it consists of well-separated, alternating layers of the complex cation  $[Ag(\mathbf{2})]^+$  and free anion  $NO_3^-$  in the lattice. In the complex ion  $[Ag(\mathbf{2})]^+$ , the  $Ag^+$  ion is  $\sigma$ -coordinated to four nitrogen atoms of the ligand **2** in a distorted-tetrahedral geometry (Fig. 2). The average distance (2.457(2) Å) of Ag–N is slightly longer than that found in  $[Ag\{N,N'\text{-bis}(2\text{-pyridylmethylene})\text{-}2,2'\text{-(ethylenedioxy)bis(ethylamine)}\}][BF_4]$  (2.331(6) Å) [27]. The twisting as expressed by the torsion angles between the naphthalene rings of  $82.6(3)^\circ$  is larger than those found in **1** ( $70.2(3)^\circ$ ), and (*R*)-2,2'-diamino-1,1'-binaphthyl ( $63.9(6)^\circ$ ) [25].



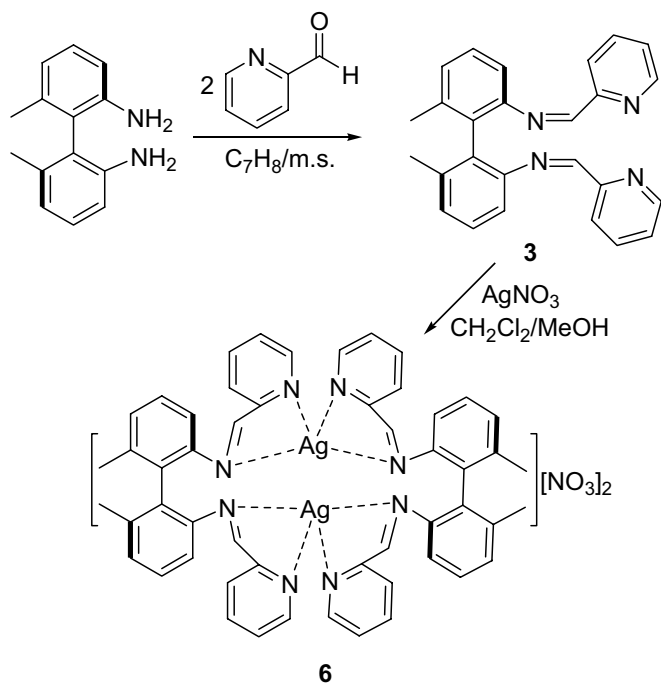
Scheme 1.

The single-crystal structure of complex **6** shows that it consists of well-separated, alternating layers of the complex cation  $[\text{Ag}_2(\mathbf{3})_2]^{2+}$  and two free anions  $\text{NO}_3^-$  with two  $\text{H}_2\text{O}$  molecules of solvent in the lattice. Coordination of two ligands **3** around two silver(I) cations results in the formation of  $[\text{Ag}_2(\mathbf{3})_2]^{2+}$  as a *P* double helix (Figs. 3a and 3b). Each silver(I) center is four-coordinate pseudo-tetrahedral, bound to two pyridylimine units, each of which is approximately planar with pyridyl-imine torsion angles in the range  $0.1$ – $7.0^\circ$ . The phenyl units are twisted with respect to the imine group with torsion angles in the range  $42.9$ – $52.9^\circ$ , and the twisting between the phenyl rings of about  $74^\circ$  is smaller than that found in (*R*)-2,2'-diamino-6,6'-dim-

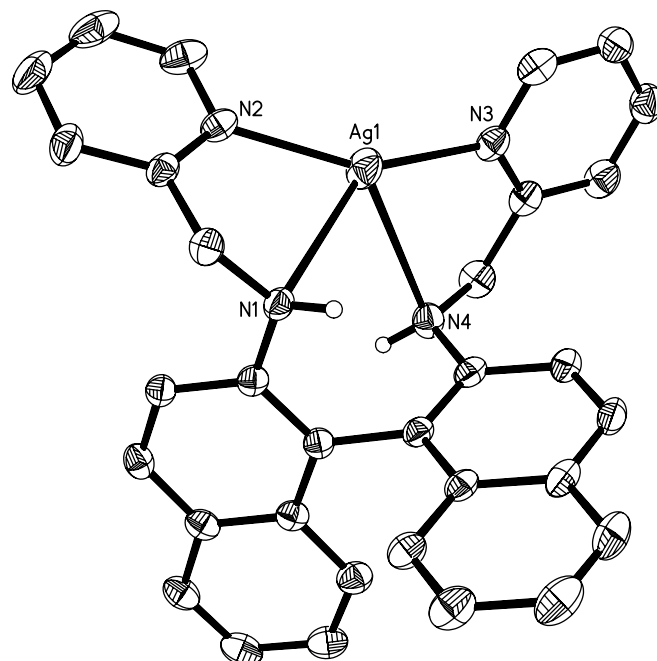
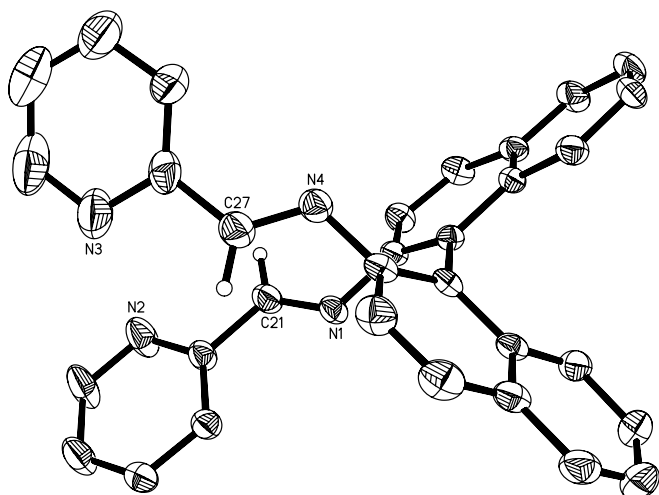
ethylbiphenyl ( $87.5(8)^\circ$ ) [28]. The combination of these twists gives rise to the formation of the double helical structure, the chirality of the helical arrays being prescribed by the chiral twist inherent in the biphenyl unit. The two silver(I) centers within the helical dications are separated by  $3.687(5)$  Å. The average distance ( $2.359(3)$  Å) of Ag–N is shorter than that found in **5** ( $2.457(2)$  Å), and is slightly longer than that found in  $[\text{Ag}\{N,N'$ -bis(2-pyridylmethylene)-2,2'-(ethylenedioxy)bis(ethylamine)\}][\text{BF}\_4] ( $2.331(6)$  Å) [27].

The single-crystal structure of complex **7** shows that it consists of well-separated, alternating layers of three complex cations  $[\text{Ag}_2(\mathbf{1})_2]^{2+}$  and two anions  $[\text{Ag}(\text{NO}_3)_3(\text{CH}_3\text{OH})]^{2-}$

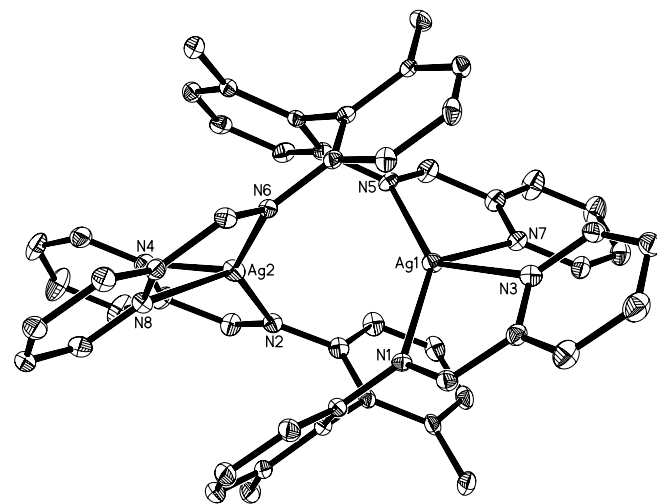
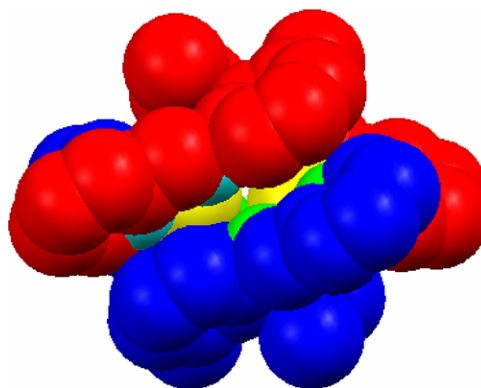




Scheme 2.

Fig. 2. Molecular structure of the cation  $[Ag_2(3)]^+$  in **5** (thermal ellipsoids drawn at the 35% probability level).Fig. 1. Molecular structure of **1** (thermal ellipsoids drawn at the 35% probability level).

and two free anions  $NO_3^-$  with two  $CH_3OH$  molecules of solvent in the lattice. Similar to the cation  $[Ag_2(3)_2]^{2+}$  in **6**, the cation  $[Ag_2(1)_2]^{2+}$  is a dinuclear double helicate (Fig. 4a), and the coordination of two ligands **1** around two silver(I) tetrahedral ions results in the formation of a *P* double helix (Fig. 4b). Each silver(I) center is four-coordinate pseudo-tetrahedral, bound to two pyridylimine units, each of which is approximately planar with pyridyl-imine torsion angles in the range 2.1–9.7°. The naphthylene units are twisted with respect to the imine group by 34.1–44.6°, and the twisting between the naphthylene rings of torsion angles (68.6(8)° and 73.2(8)°) are smaller than that (82.6(3)°) found in **5**,

Fig. 3a. Molecular structure of the cation  $[Ag_2(3)_2]^{2+}$  in **6** (thermal ellipsoids drawn at the 35% probability level).Fig. 3b. Space-filling diagram of the cation *P*- $[Ag_2(3)_2]^{2+}$  in **6**.

and close to that found in **1** (70.2(3)°). The two silver(I) centers within the helical dication are separated by 3.760(15) Å, which is slightly longer than that found in **6** (3.687(5) Å). The average distance (2.333(10) Å) of Ag–N is shorter than those found in **5** (2.457(2) Å) and **6** (2.359(3) Å), and is close to that found in [Ag{*N,N'*-bis(2-pyridylmethylene)-2,2'-(ethylenedioxy)bis(ethylamine)}][BF<sub>4</sub>] (2.331(6) Å) [27]. These structural data are very close to those found in [Ag<sub>2</sub>(C<sub>32</sub>H<sub>22</sub>N<sub>4</sub>)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> [26].

In the anion [Ag(NO<sub>3</sub>)<sub>3</sub>(CH<sub>3</sub>OH)]<sup>2-</sup>, the three oxygen atoms of NO<sub>3</sub><sup>-</sup> and one oxygen atom of CH<sub>3</sub>OH are σ-coordinated to the Ag<sup>+</sup> cation in a C<sub>3v</sub> geometry (Fig. 4c). The average distance (2.485(2) Å) of Ag–O(NO<sub>3</sub><sup>-</sup>) is slightly longer than that (2.28(3) Å) of Ag–O(CH<sub>3</sub>OH), and close to that (Ag–O(NO<sub>3</sub><sup>-</sup>)) found in {[Ag<sub>3</sub>(1,3,5-tri(pyraol-1-yl)benzene)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>NO<sub>3</sub>]<sub>n</sub>} (2.515(5) Å) [29].

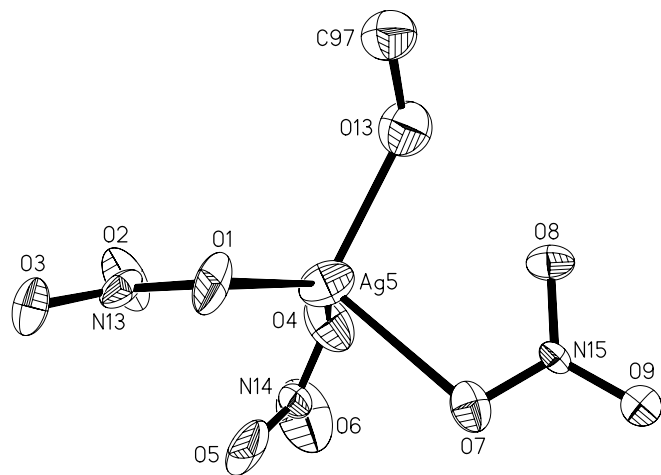


Fig. 4c. Molecular structure of the anion [Ag(NO<sub>3</sub>)<sub>3</sub>(CH<sub>3</sub>OH)]<sup>2-</sup> in **7** (thermal ellipsoids drawn at the 35% probability level).

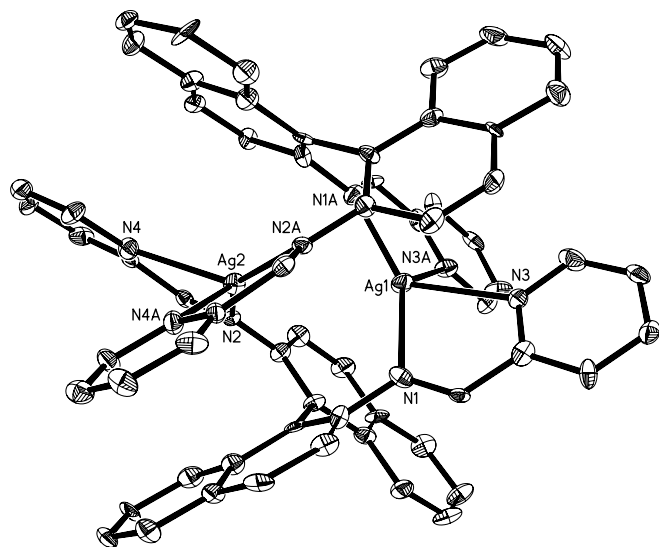


Fig. 4a. Molecular structure of the cation [Ag<sub>2</sub>(**1**)<sub>2</sub>]<sup>2+</sup> in **7** (thermal ellipsoids drawn at the 35% probability level).

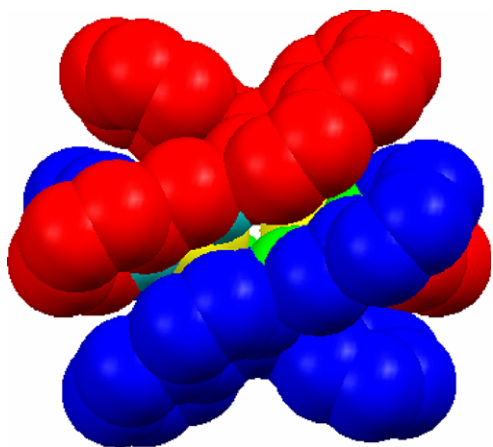


Fig. 4b. Space-filling diagram of the cation *P*-[Ag<sub>2</sub>(**1**)<sub>2</sub>]<sup>2+</sup> in **7**.

#### 4. Conclusions

In conclusion, a series of new chiral Ag(I) complexes with novel features have been synthesized from the reactions between AgNO<sub>3</sub> and chiral N<sub>4</sub> ligands, (*R*)-*N,N'*-bis(pyridin-2-ylmethylene)-1,1'-binaphthyl-2,2'-diimine (**1**), (*R*)-*N,N'*-bis(pyridin-2-ylmethyl)-1,1'-binaphthyl-2,2'-diamine (**2**), and (*R*)-*N,N'*-bis(pyridin-2-ylmethylene)-6,6'-dimethylbiphenyl-2,2'-diimine (**3**). Rigidity plays an important role in the formation of the helicate silver(I) complexes. For example, ligand **1** induces a dinuclear double helicate, while ligand **2** affords a mononuclear single helicate. Further efforts will focus on the applications of these silver(I) complexes toward asymmetric reactions and the exploration of new silver(I) complexes based on chiral N<sub>4</sub> ligands.

#### 5. Supplementary material

CCDC 644762, 644763, 644764 and 644765 contain the supplementary crystallographic data for **1**, **5**, **6** and **7**. 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, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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