The synthesis and structural characterisation of helical silver(I) complexes with short bis(pyridylimine) ligands

Guo Dong, He Cheng, Duan Chun-Ying,* Qian Chun-Qi and Meng Qing-Jin*

Coordination Chemistry Institute, The State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China. E-mail: duancy@nju.edu.cn

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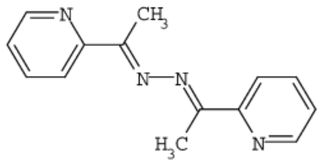
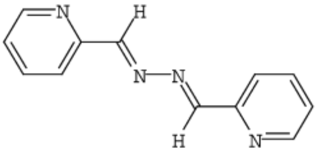
Three new disilver(I) double helicate complexes $[Ag_2L_2][ClO_4]_2$ (**1**), $[Ag_2L_2][BF_4]_2$ (**2**) $[Ag_2L_2][NO_3]_2$ (**3**) and a polymeric monohelical species $[Ag_2L'_2][BF_4]_2$ (**4**) have been generated *via* a self-assembly procedure to establish the effect of a side-chain on the subtle metal–ligand coding. The ligands, $L = (C_5H_4N)C(CH_3)$=N–N=$C(CH_3)(C_5H_4N)$ and $L' = (C_5H_4N)CH$=N–N=$CH(C_5H_4N)$, were both readily prepared imine-based systems, in which the two bis-bidentate chelating units are separated by a single bond. Complexes **1**, **2** and **3** adopt a double helical architecture, in which each silver centre is bound to two pyridylimine units in a distorted tetrahedral coordination geometry. Complex **4** is formed as an infinite monohelical polymer in which each silver centre is coordinated in a distorted tetrahedral geometry by two bidentate binding units from different ligands and the ligands are in turn coordinated to two silver(I) centres. While the two pyridylimine units of the ligand L are able to twist both in its free form and in the double helicates **1**, **2** and **3**, ligand L′ presents a planar conformation in both the free ligand and its monohelical complex **4**. It is speculated that the arrangement of the two pyridylimine units around the N–N bond is essential to encode for a double helicate. Intra- and inter-molecular non-covalent interactions are found to stabilize the polymer **4** and provide opportunities for complexes **1**, **2** and **3** to crystallize in different space groups.

Helical complexes have elegantly illustrated how the formation of specific architecturally complex assemblies can be directed by the interplay between relatively simple parameters, such as the stereoelectronic preference of the metal and the disposition of binding sites of helicands (helicating ligands).[1] A helicate is classically described as a discrete helical supramolecular complex composed of one or more covalent organic strands wrapped around a series of ions defining the helical axis. Many helicates are derived from ligands that are obviously partitioned into two distinct bidentate binding sites with a spacer linking them together. For a dinuclear double helical architecture, it is postulated[2–4] that the chosen spacer should firstly have enough rigidity to sterically prevent the two metal binding sites from coordinating to a single metal centre and secondly should introduce enough flexibility into the ligand backbone to permit the ligands to wrap around the metal–metal axis. Chiral helices will result only when the two metal ions display the same absolute configurations.[5,6] It is expected that the ligand used to build double helicates needs to be able to transmit the chirality from one metal centre to another.

To establish our approach, ligand L with two pyridylimine sites connected by a single bond was chosen to address the challenge of creating double helical architectures. It should be noted that this is the shortest possible imine-based ligand system of this type.[7–9] The rigidity of the ligand and the close proximity of the two metal centres seem unfavourable for double helicate formation. In fact, this is the first description of double metallo-helicates formed from such a system in which the two binding sites are directly connected. A related system was reported by Ziessel *et al.*,[9] in which the two nitrogen donors were separated by a single carbon atom with an N···N separation of *ca.* 2.3 Å. As a comparison, the silver(I) complex of Ligand L′ is also reported to study the side-chain effect on the subtle metal–ligand coding.



L



L′

Results and discussion

Synthesis and crystal structure of ligand L

The ligands L and L′ were prepared by mixing hydrazine hydrate with 2-acetylpyridine and 2-pyridinecarboxaldehyde, respectively.[10] The simplicity of the syntheses and the high yields in a single step from inexpensive commercially available reagents allow us the possibility to systematically probe the effects of modifying the ligand backbone and attempt to control the precise topography (or microarchitecture) of the arrays.[3,8,11] Elemental analyses, IR and NMR spectra confirm the formation of the given ligands.

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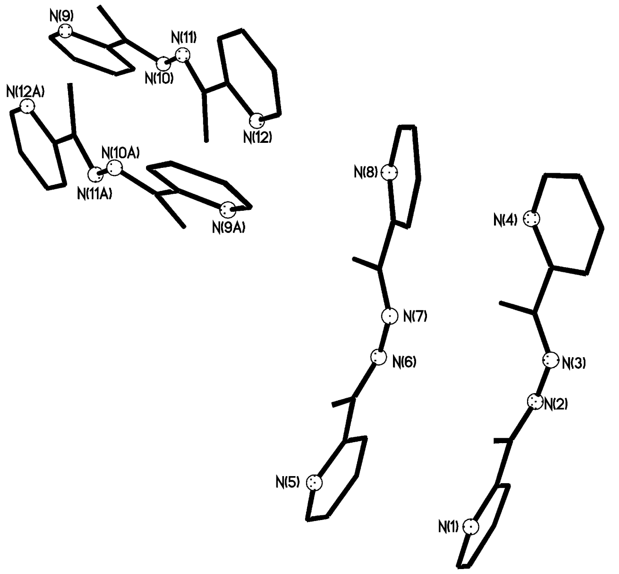

Fig. 1 Crystal structure of the ligand L. Symmetry code A: $1-x$, $2-y$, $1-z$.

Ligand L crystallizes in a monoclinic system with three independent molecules in the asymmetric unit (Fig. 1). The pyridylimine units adopt a *transoid* configuration to minimize unfavourable electronic interactions between the lone pairs of N(pyridyl) and N(imine). However, in the presence of metal ions, the pyridine rings rotate by 180° with respective to the Ar–C bond, placing the two nitrogen atoms of each pyridylimine moiety on the same side. Thus, it can function as a bis-bidentate ligand. Though non-planar as a whole, each molecule comprises two planar pyridylimine fragments. A considerable distribution in the dihedral angles between the two pyridylimine units, ranging from 59 to 38° (with an average of *ca.* 47°), is observed. It seems that the steric hindrance of closely spaced methyl groups and the repulsion of the lone pairs of the imino nitrogen atoms play an important part in the instability of the planar conformation of the free ligand L. Consequently, ligand L appears to be able to accept various dihedral angles between two pyridylimine units. It is suggested that the non-planarity of the two pyridylimine fragments is essential in such a rigid system to encode for a tetrahedral metal centre in a double helical arrangement.

Ligand L'[10b] is planar with the midpoint of the N–N bond lying on an inversion centre. As in ligand L, the two nitrogen donors of each pyridylimine unit also adopt a *transoid* configuration and act as a bis-bidentate ligand in the presence of metal ions. However, it should be noted that such a fully conjugated planar system seems unfavourable for double helicate formation.

As expected, molecules of the two ligands L and L' crystallize in different conformations. While adjacent molecules of ligand L' are organized into one-dimensional chains by strong π–π stacking interactions, ligand L forms dimers with an adjacent molecule by weak π–π stacking interactions of the aromatic rings. In the latter, the shortest inter-planar atom···atom separations and dihedral angles are 3.63 Å (4.1°), 3.51 Å (20.5°) and 3.47 Å (40°) for the stacked pairs I and III, II and IV, as well as VI and VIA (symmetry code A: $1-x$, $2-y$, $1-z$), respectively.† These distances are within the common ranges of typical stacked interactions,[12] however it should be noted that the centre-to-centre separations of these stacked pairs are 3.94 Å, 4.07 Å and 4.76 Å, respectively, indicating that these interactions are quite weak. Generally, these stacking interactions only present in the solid state, however, in a number of multinuclear complexes and polymers[4b,13,14] they contribute to the formation and stability of the architectures even in solution. By analogy, we assume that the differences exhibited in the crystal structures by these two ligands might give rise to different metal-ligand interactions and so different products upon complexation.

Double helical complex 1

Reaction of ligand L with one equivalent of $AgClO_4$ in methanol yields a yellow powder. Elemental analysis, IR and NMR spectra were consistent with the formation of the expected silver complex $[Ag_2L_2(ClO_4)_2]$. The ESI-MS confirmed the stoichiometry with the main peak at $m/z = 790.7$ corresponding to $[Ag_2L_2(ClO_4)]^+$.[15] Association between the cationic helicates and various counter anions (*e.g.*, $CF_3SO_3^-$, PF_6^-, BF_4^-, ClO_4^-) are very common in ESI-MS and have been tentatively attributed to electrostatic interactions.[16] The X-ray structural analysis on suitable crystals grown from acetonitrile indicated that complex **1** is a dimeric double helicate (Fig. 2); with each silver(I) centre coordinated to two pyridylimine moieties from each of the two ligands. Two silver(I) ions are doubly bridged by the N–N groups with a separation of 4.87 Å. This Ag···Ag contact is not typical of those observed in many polynuclear disilver(I) complexes and is not thought to be indicative of any particular intermetallic electronic interaction.[17] Each silver(I) ion coordinates to two imine (2.36–2.44 Å) and two pyridyl (2.19–2.29 Å) nitrogens, forming a distorted tetrahedral geometry. Weak coordination bonds between the silver(I) atoms and ClO_4^- anions were found to stabilize the heavily distorted tetrahedron of the silver(I) atoms (Table 1).

An interesting feature of the dication is that the ligand spans both the silver ions, but does not wrap around the metal–metal axis as demonstrated by the longer bis(pyridylimine) ligands.[4,8] One of the two ligands passes above the Ag(I)–Ag(I) axis and the other goes beneath, with the $[Ag_2L_2]^{2+}$ cation appearing more like a box than a double helix. The rigidity of the imine-based ligand and the close distance of the silver(I) cations seem unfavourable for helicate formation. In fact, this is the first description of double metallo-helicates formed from the ligands in which two binding sites are connected by a single bond. In both double and triple helicates there does not appear to be a strong relationship between their formation and the rigidity/flexibility of spacers. However, it should be noted that coordination to the metal centres forces interannular twisting between the two pyridine rings in the ligand (with dihedral angles of *ca.* 82°), resulting in the formation of a double helical array. Similar ligand twisting in double and triple helical architectures indicates that non-planarity about the N–N bond between the two pyridylimine units is essential for such a ligand to encode for a tetrahedral coordination about the metal ion in the double helical form and an octahedral coordination around the metal ions in the triple helical form.

It is also interesting to note that there are no obvious intermolecular π–π interactions involving pyridine rings. The shortest intermolecular atom···atom separation (3.23 Å) was found to be between the methyl groups and adjacent pyridine rings. This result indicates that the presence of the methyl groups can efficiently reduce the possibility of intermolecular π–π interactions between adjacent pyridine rings. The C···Py separation related to the carbon atoms C(102) and the pyridine ring IA (symmetry code A: $1-x$, $-y$, $-z$) is *ca.* 3.56 Å,

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† For all ligands and complexes: plane I is defined by atoms N(1), C(1), C(2), C(3), C(4) and C(5); plane II is defined by atoms N(4), C(8), C(9), C(10), C(11) and C(12); plane III is defined by atoms N(5), C(13), C(14), C(15), C(16) and C(17); plane IV is defined by atoms N(8), C(20), C(21), C(22), C(23) and C(24); plane V is defined by atoms N(9), C(20), C(21), C(22), C(23) and C(24) and plane VI is defined by atoms N(10), C(32), C(33), C(34), C(35) and C(36).

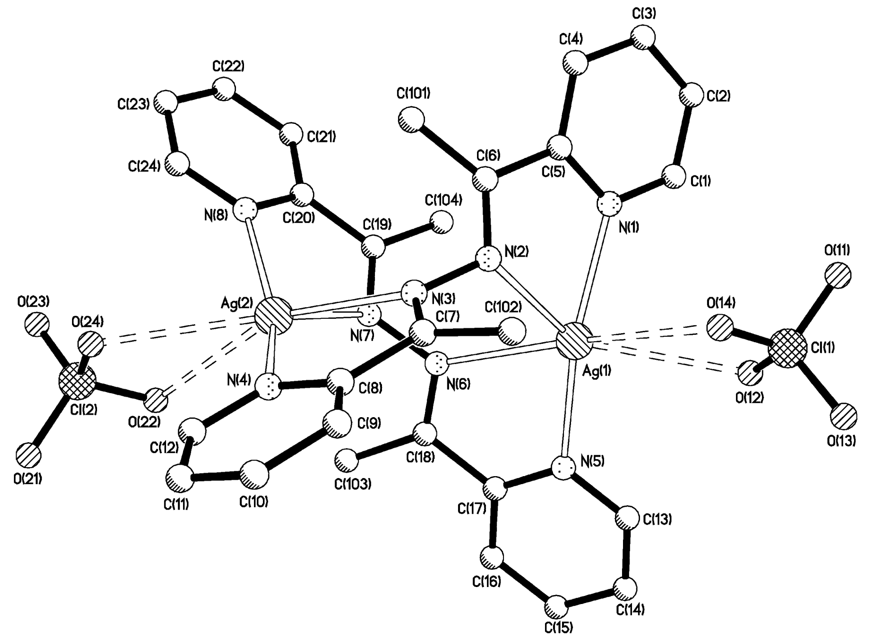

Fig. 2 Molecular structure of the double helical complex **1**.

Table 1 Selected bond distances (Å) and angles (°) of complexes **1–3**

1				**2**		**3**	
Ag(1)–N(5)	2.226(3)	Ag(2)–N(4)	2.188(2)	Ag(1)–N(1)	2.268(6)	Ag(1)–N(1)	2.347(2)
Ag(1)–N(2)	2.386(3)	Ag(2)–N(7)	2.365(3)	Ag(1)–N(3A)^a	2.466(6)	Ag(1)–N(3A)^b	2.549(2)
Ag(1)–N(1)	2.290(3)	Ag(2)–N(8)	2.275(3)	Ag(1)–N(4A)^a	2.291(6)	Ag(1)–N(4A)^b	2.323(2)
Ag(1)–N(6)	2.473(3)	Ag(2)–N(3)	2.466(3)	Ag(1)–N(2)	2.489(6)	Ag(1)–N(2)	2.457(2)
Ag(1)–O(12)	2.839(5)	Ag(2)–O(22)	2.994(5)	Ag(1)–F(1)	3.186(8)	Ag(1)–O(1)	2.657(4)
Ag(1)–O(14)	3.031(5)	Ag(2)–O(24)	2.884(5)	Ag(1)–F(2)	2.866(7)	Ag(1)–O(2)	2.793(4)
N(5)–Ag(1)–N(1)	155.0(1)	N(4)–Ag(2)–N(8)	153.5(1)	N(1)–Ag(1)–N(4A)^a	153.2(2)	N(1)–Ag(1)–N(4A)^b	153.95(8)
N(1)–Ag(1)–N(2)	69.8(1)	N(8)–Ag(2)–N(7)	70.6(1)	N(4A)–Ag(1)–N(3A)^a	69.3(2)	N(1)–Ag(1)–N(2)	67.98(7)
N(1)–Ag(1)–N(6)	110.5(1)	N(8)–Ag(2)–N(3)	111.6(1)	N(4A)–Ag(1)–N(2)^a	113.3(2)	N(1)–Ag(1)–N(3A)^b	107.84(7)
N(5)–Ag(1)–N(2)	132.2(1)	N(4)–Ag(2)–N(7)	133.4(1)	N(1)–Ag(1)–N(3A)^a	135.5(2)	N(4A)–Ag(1)–N(2)^b	133.66(7)
N(5)–Ag(1)–N(6)	70.0(1)	N(4)–Ag(2)–N(3)	70.7(1)	N(1)–Ag(1)–N(2)	68.8(2)	N(4A)–Ag(1)–N(3A)^b	66.94(7)
N(2)–Ag(1)–N(6)	78.5(1)	N(7)–Ag(2)–N(3)	78.1(1)	N(3A)–Ag(1)–N(2)^a	82.5(2)	N(3A)–Ag(1)–N(2)^b	82.32(7)

[a] Symmetry code A: $-x$, y, $-z+1/2$. [b] Symmetry code A: $1-x$, y, $-z+1/2$.

where Py is the centre of the pyridine ring. A similar C···Py contact (3.33 Å) was also found involving the methyl group C(103) and pyridine ring IVB (symmetry code B: $2-x$, $1-y$, $1-z$). These distances are shorter than the sum (3.7 Å) of the van der Waals radii of the methyl group (2.0 Å) and aromatic carbon (1.7 Å)[18], indicating a weak interaction between C–H (soft acid) and π group (soft base) as advocated by Nishio.[19] Such C–H···π intermolecular interactions link the double helicates one-by-one to form one-dimensional infinite chains (Fig. 3).

Double helical complexes 2 and 3

Since the helicates are ionic species, weak electrostatic interactions driven by the anions are also an essential factor influencing molecular formation and crystallization. Treatment of L with one equivalent $AgBF_4$ or $AgNO_3$ in methanol yielded yellow powders. ESI-MS in acetonitrile–methanol solution revealed the presence of one main peak corresponding to $[Ag_2L_2(BF_4)]^+$ ($m/z = 778.9$) for **2**, and $[Ag_2L_2(NO_3)]^+$ ($m/z = 753.7$) for **3**, indicating the formation of dinuclear species.

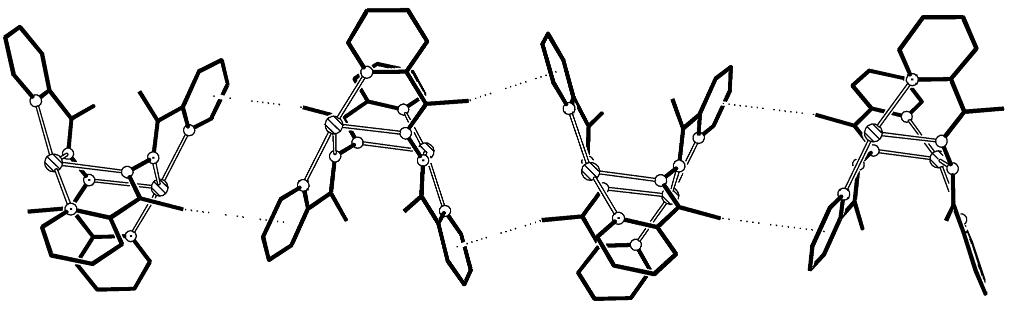

Fig. 3 View of the one-dimensional chain in complex **1** showing intermolecular C–H···π interactions. Hydrogen atoms and anions are omitted for clarity.

While complex **1** crystallized in a triclinic crystal system, complexes **2** and **3** adopt a monoclinic lattice. As shown in Fig. 4 and 5, complexes **2** and **3** are isostructural double helices with the equivalent AgL fragment inter-related by the C_2 axis. Each silver(I) centre is bound by two pyridylimine units to attain a distorted tetrahedral coordination geometry with an Ag···Ag separation of *ca.* 4.85 Å for both **2** and **3**. The Ag–N (pyridyl) distances (Table 1) are *ca.* 2.3 Å and Ag–N (CH=N) distances *ca.* 2.5 Å on average. Weak coordination between the silver atoms and the BF_4^- or NO_3^- anions was also found to stabilize the heavily distorted conformation of the silver(I) atoms. As expected, coordination to the metal centre forces an interannular twisting between the two pyridine rings, which leads to the formation of double helical arrays with the dihedral angles of the two pyridylimine units in one ligand being *ca.* 83 and 84°, for complexes **2** and **3**, respectively, which is consistent with that of complex **1**.

In the crystal of complex **2**, the pyridine ring I stacks with the symmetry related pyridine ring IB (symmetry code B: $0.5-x$, $1.5-y$, $1-z$) by weak interactions, which link the cations to form one-dimensional infinite chains. The shortest interplanar atom···atom separation and the centre···centre separation between the stacked pair are *ca.* 3.49 and 3.64 Å, respectively, which is in agreement with results found in related

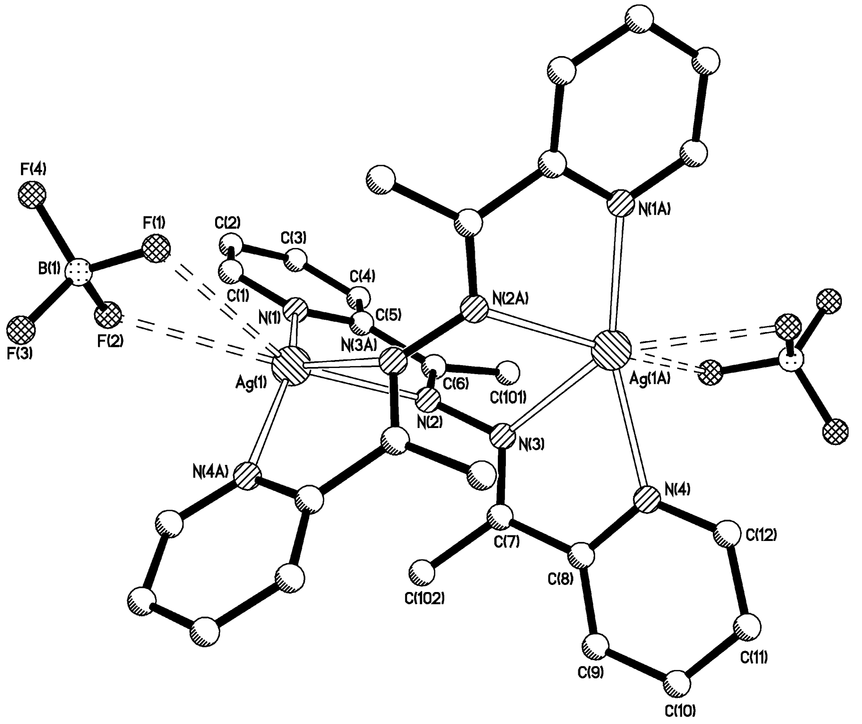

Fig. 4 Molecular structure of the double helical complex **2**. Symmetry code A: $1-x$, y, $0.5-z$.

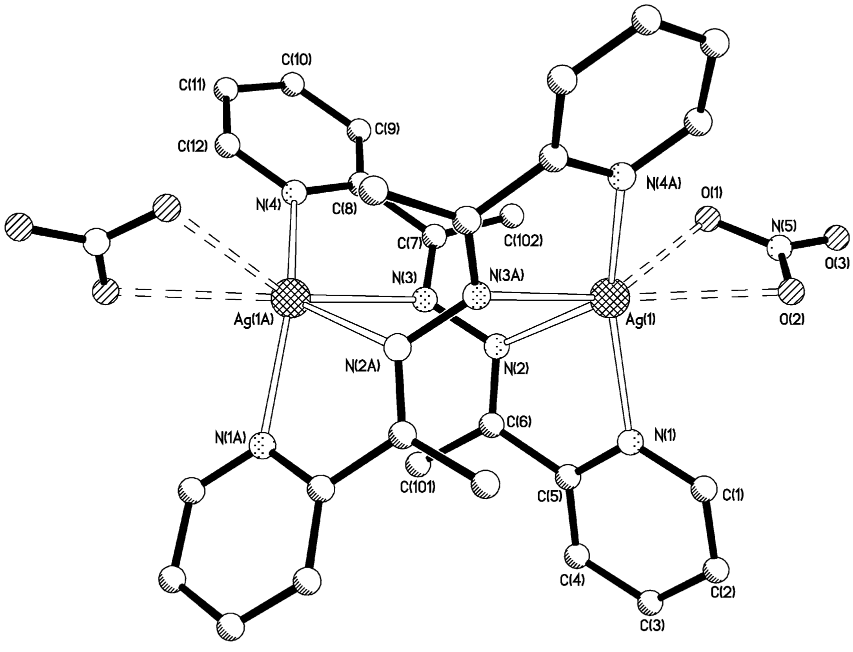

Fig. 5 Molecular structure of the double helical complex **3**. Symmetry code A: $-x$, y, $0.5-z$.

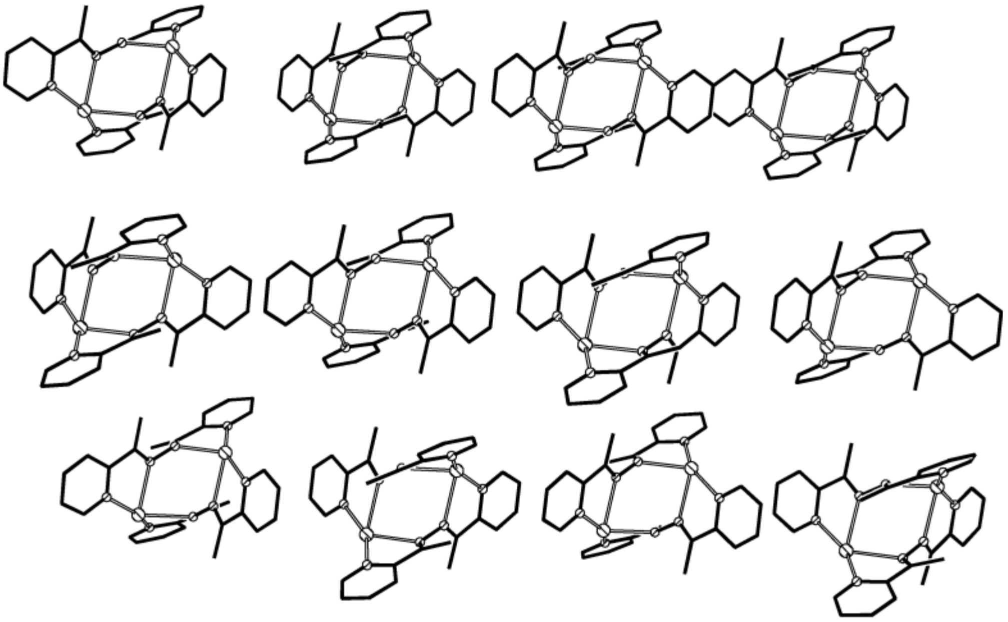

Fig. 6 View of the two-dimensional network in complex **2** showing intermolecular interactions in the crystal packing.

complexes.[13] Weak C–H···π interactions were also found between the methyl carbon atom C(101) and the adjacent pyridine ring IIC (symmetry code C: $-x$, $1-y$, $1-z$), with a C(101)···Py separation of *ca.* 3.48 Å, where Py is the centre of the pyridine ring. Through these C–H···π interactions, the one-dimensional infinite chains expand into a two-dimensional supramolecular network (Fig. 6). Molecules of **3** crystallize in a similar form to that of complex **2**. The shortest interplanar atom···atom separation for the stacked pairs (*ca.* 3.64 Å) and C···Py separations (*ca.* 3.71 Å) of the weak C–H···π interactions are slightly longer than those in the crystal packing of complex **2**, showing that little difference exists between the two crystal structures of **2** and **3** because of the weak electrostatic interactions with the anions.

Monohelical complex 4

The reaction of ligand L′ with $AgBF_4$ in ethanol gave the yellow product **4**. Elemental analysis, IR and NMR spectra were consistent with the formation of a complex with a one-to-one stoichiometry, but the product demonstrated very poor solubility. Suitable crystals for X-ray structural analysis were grown from a layered methanolic solution of $AgBF_4$ and ligand L′ in DMF. Complex **4** exhibited a very different structure from that of complexes **1**–**3** being an infinite monohelical chain, which coils to form a square channel (Fig. 7). Each silver centre is bound to two bis-bidentate ligands in a distorted tetrahedral geometry (Table 2) and the ligands are in turn coordinated to two silver(I) centres. The helical pitch, given by one full rotation around the 2_1 screw axis, is 13.02 Å (the unit cell length along the crystallographic *b* axis). Since the crystal adopts the $P2_1$ space group, the axis of the helix is crystallographically at (1/2, *y*, 1/2) with Ag···Ag separations being 5.61 Å [Ag(1)···Ag(2)] and 5.90 Å [Ag(1A)···Ag(2)] ($-x+1$, $y-1/2$, $-z+1$). The ligands adopt coplanar conformations with dihedral angles between the two pyridylimine units being *ca.* 5°. It should be noted that *intramolecular* face-to-face π–π stacking interactions appear to stabilize the infinite chains. The pyridine rings III and IIV within one ligand are parallel to the related pyridine rings IVB and IIIB (dihedral angle 0.7°, symmetry code B: $-x+1$, $y+1/2$, $-z+1/2$) and the separation between the rings is 3.40 Å, indicating a strong π–stacking interaction.[12] At the same time, intermolecular π–π stacking interactions between helical chains are observed, with two pyridine rings from adjacent chains being separated by 3.52 Å and forming two dimensional sheets.

Conclusions

The first examples of double helicates derived from the possible shortest bis(pyridylimine) based rigid ligand are achieved *via* self-assembly synthetic procedures. Although the rigidity of the ligand and the closeness of the silver cations might contribute to the instability of the double helical structure, the possibility of variable dihedral angles between two pyridylimine units in ligand L provides an opportunity to generate double helicates. The investigation of side-chain effects with

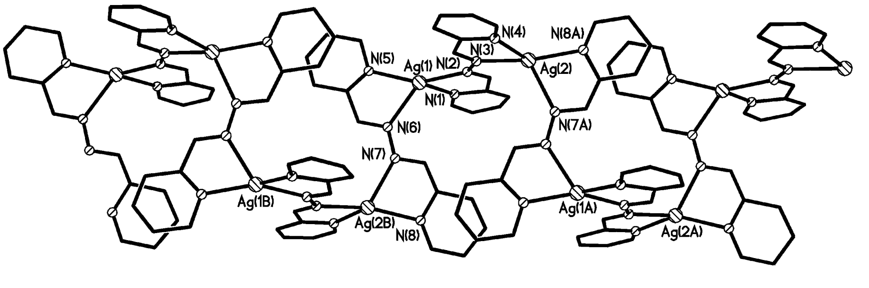

Fig. 7 View of crystal packing along the crystallographic *b* axis showing the layers of helices **4** and the channels present in the structure. Hydrogen atoms and anions are omitted for clarity. Symmetry code A: $1-x$, $0.5-y$, $1-z$; B: $1-x$, $0.5+y$, $1-z$.

Table 2 Selected bond distances (Å) and angles (°) of complex **4**

Ag(1)–N(5)	2.227(10)	Ag(1)–N(2)	2.287(9)
Ag(1)–N(1)	2.262(9)	Ag(1)–N(6)	2.382(8)
Ag(2)–N(3)	2.371(8)	Ag(2)–N(8A)[a]	2.309(10)
Ag(2)–N(4)	2.300(11)	Ag(2)–N(7A)[a]	2.450(8)
N(5)–Ag(1)–N(2)	147.1(3)	N(5)–Ag(1)–N(1)	133.3(3)
N(1)–Ag(1)–N(2)	73.6(3)	N(5)–Ag(1)–N(6)	68.9(3)
N(2)–Ag(1)–N(6)	125.8(3)	N(1)–Ag(1)–N(6)	110.2(3)
N(3)–Ag(2)–N(8A)[a]	148.2(3)	N(4)–Ag(2)–N(3)	75.7(3)
N(8A)–Ag(2)–N(7A)[a]	75.7(3)	N(3)–Ag(2)–N(7A)[a]	119.0(3)
N(8A)–Ag(2)–N(4)[a]	126.0(4)	N(7A)–Ag(2)–N(4)[a]	115.3(3)

[a] Symmetry code A: $1 - x$, $-0.5 + y$, $1 - z$.

ligands L and L′ and the related double and single helices demonstrate that the presence of methyl groups is an essential factor for the free ligand L adopting a non-planar configuration. It is also interesting to note that the presence of a methyl group in the ligand backbone can also weaken the potential intermolecular interactions between pyridine rings, which might be an important factor influencing the molecular structure and crystal lattice adopted.

Experimental

Caution! Perchlorate salts are potentially explosive and should only be handled in small quantities.

General

All chemicals obtained from commercial sources were of reagent grade quality and used without further purification. Elemental analyses (C, H and N) were carried out on a Perkin–Elmer 240 analyzer. IR spectra were recorded on a VECTOR 22 Bruker spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region. ^{1}H NMR spectra for ligand L and complex **4** were recorded on a Bruker DP300 spectrometer, for complexes **1**–**3** on a DRX500 Bruker spectrometer at 298 K and electrospray mass spectra on a LCQ system (Finnigan MAT, USA) using methanol as the mobile phase.

Preparations

Ligand L. Hydrazine hydrate (85% aqueous, 0.5 g, 8.5 mmol) and 2-acetylpyridine (2.5 g, 21 mmol) were mixed in methanol (15 ml) and then refluxed for 3 h. The solution was evaporated to 5 ml, and the resulting yellow precipitate was collected by filtration and dried *in vacuo* (1.5 g, 6.3 mmol, yield 74%). Found: C, 70.4; H, 5.9; N, 23.2. Calcd for $C_{14}H_{14}N_4$: C, 70.6; H, 5.9; N, 23.5%. ^{1}H NMR [300 MHz, $(CD_3)_2SO$]: δ 2.26 (s, 6H, CH), 7.45 (t, 2H, *J* 4.5 Hz, py), 7.87 (t, 2H, *J* 7.5 Hz, py), 8.16 (d, 2H, *J* 7.5 Hz, py), 8.63 (d, 2H, *J* 4.6 Hz, py). IR(KBr): 3389.8(w), 3188.8(w), 1652.5(m), 1613.7(s), 1561.8(s), 1464.0(s), 1432.9(s), 1356.7(s), 1101.3(s), 780.4(s), 739.1(s), 645.0(m), 570.1(m).

Complex 1. Ligand L (0.05 g, 0.2 mmol) and $AgClO_4$ (0.06 g, 0.2 mmol) were dissolved in ethanol (25 ml) and mixed for 0.5 h, giving a yellow solution. Upon cooling a yellow precipitate was obtained, which was collected by filtration and dried *in vacuo* (0.08 g, 0.08 mmol, yield 75%). Found: C, 39.3; H, 4.3; N, 11.5. Calcd for $Ag_2C_{28}Cl_2H_{28}N_8O_8{\cdot}2C_2H_5OH$: C, 39.1; H, 4.1; N, 11.4%. ^{1}H NMR [500 MHz, $(CD_3)_2SO$]: δ 2.30 (s, 6H, CH), 7.55 (t, 2H, *J* 5.0 Hz, py), 7.97 (t, 2H, *J* 7.8 Hz, py), 8.16 (d, 2H, *J* 7.5 Hz, py), 8.70 (d, 2H, *J* 4.0 Hz, py). IR(KBr): 3447.5(w), 3054.8(w), 1613.7(m), 1583.1(m), 1563.1(m), 1463.5(s), 1434.9(m), 1361.4(s), 1245.8(m), 1143.7(s), 1088.2(s), 1044.6(m), 991.6(m), 779.5(s), 741.2(m), 623.0(s), 570.1(m). Crystals suitable for X-ray diffraction were obtained by slow evaporation of an acetonitrile solution of complex **1**.

Complex 2. Ligand L (0.12 g, 0.5 mmol) and $AgBF_4$ (0.10 g, 0.51 mmol) were dissolved in ethanol (25 ml) and mixed for 0.5 h, giving a yellow precipitate that was collected by filtration and dried *in vacuo* (0.16 g, 0.19 mmol, 74%). Found: C, 39.1; H, 3.2; N, 12.8. Calcd for $Ag_2B_2C_{28}F_8H_{28}N_8$: C, 38.8; H, 3.3; N, 12.9%. ^{1}H NMR [500 MHz, $(CD_3)_2SO$]: δ 2.30 (s, 6H, CH), 7.57 (q, 2H, *J* 6.3 Hz, py), 7.99 (d, 2H, *J* 7.8 Hz, py), 8.15 (d, 2H, *J* 8.0 Hz, py), 8.72 (d, 2H, *J* 5.0 Hz, py). IR(KBr): 3448.6(w), 3054.4(w), 1613.5(m), 1583.4(s), 1563.2(m), 1463.5(s), 1434.8(m), 1361.2(s), 1303.8(w), 1245.3(w), 1043.2(s), 991.9(m), 779.4(s), 740.9(s), 621.5(m), 570.4(m), 521.3(m). Crystals suitable for X-ray diffraction were obtained by slowly diffusing diethyl ether into an acetonitrile solution.

Complex 3. Ligand L (0.05 g, 0.2 mmol) and $AgNO_3$ (0.034 g, 0.2 mmol) were stirred in ethanol (25 ml) for 0.5 h, giving a yellow precipitate that was collected by filtration (0.07 g, 0.08 mmol, yield 81%). Found: C, 42.3; H, 4.2; N, 16.7. Calcd for $Ag_2C_{28}H_{28}N_{10}O_6{\cdot}CH_3CN{\cdot}C_2H_5O$: C, 42.7; H, 4.0; N, 17.1%. ^{1}H NMR [500 MHz, $(CD_3)_2SO$]: δ 2.30 (s, 6H, CH), 7.56 (q, 2H, *J* 5.5 Hz, py), 7.98 (h, 2H, *J* 1.5 Hz, py), 8.16 (d, 2H, *J* 8.0 Hz, py), 8.71 (d, 2H, *J* 4.0 Hz, py). IR(KBr): 3447.2(w), 3054.8(w), 1613.6(w), 1583.2(m), 1562.7(m), 1463.5(m), 1434.0(m), 1384.4(s), 1361.0(s), 1303.3(m), 1100.4(m), 1043.4(m), 991.6(m), 825.1(w), 779.5(s), 740.6(m), 621.3(w), 570.0(w). Recrystallization of the complex from an acetonitrile solution by diffusion of diethyl ether afforded crystals from which we confirmed the structure by X-ray crystallography.

Complex 4. Ligand L′ (0.11 g, 0.5 mmol) and $AgBF_4$ (0.10 g, 0.51 mmol) were dissolved in ethanol (25 ml), and after stirring for 0.5 h the yellow precipitate was isolated by filtration and dried *in vacuo* (0.16 g, 0.4 mmol, yield 80%). (Note the product could not be dissolved in common organic solvents). Found: C, 35.1; H, 2.3; N, 13.7. Calcd for $AgBC_{12}F_4H_{10}N_4$: C, 35.6; H, 2.5; N, 13.8%. ^{1}H NMR [300 MHz, $(CD_3)_2SO$]: δ 7.70 (t, 2H, *J* 5.4 Hz, py), 8.03 (d, 2H, *J* 6.3 Hz, py), 8.11 (t, 2H, *J* 7.8 Hz, py), 8.70 (d, 2H, *J* 4.8 Hz, py), 8.95 (s, 2H, CH=N). IR(KBr): 3448.4(w), 3053.5(w), 1631.8(m), 1585.4(s), 1566.4(m), 1475.5(m), 1433.0(s), 1304.4(m), 1055.5(s), 955.0(m), 774.3(s), 700.7(m), 503.5(m). Crystals suitable for X-ray diffraction were obtained by layering a solution of $AgBF_4$ in methanol over a solution of L′ in DMF and keeping in the dark for one week.

Crystallography

Parameters for data collection and refinement of the four complexes and ligand L are summarized in Table 3. Intensities for ligand L as well as complex **1** were collected on a Siemens

Table 3 Crystallographic data for ligand L and complexes **1**–**4**

	L	**1**	**2**	**3**	**4**
Molecular formula	$C_{14}H_{14}N_4$	$Ag_2C_{28}C_{l2}H_{28}N_8O_8$	$Ag_2B_2C_{28}F_8H_{28}N_8$	$Ag_2C_{28}H_{28}N_{10}O_6$	$Ag_2B_2C_{28}F_8H_{26}N_{10}$
M	238.29	891.22	865.94	816.34	891.95
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2(1)/c$	$P\bar{1}$	$C2/c$	$C2/c$	$P2(1)$
a/Å	8.5633(9)	8.6444(17)	25.648(4)	20.017(4)	10.639(4)
b/Å	18.779(2)	13.663(3)	8.5664(6)	9.1800(18)	13.019(4)
c/Å	24.041(3)	14.079(3)	18.328(7)	17.192(3)	13.141(5)
$\alpha/°$	90.00	90.29(3)	90	90	90
$\beta/°$	96.154(2)	104.04(3)	126.157(14)	94.25(3)	102.69(2)
$\gamma/°$	90.00	107.57(3)	90	90	90
U/Å^3	3843.9(7)	1532.4(5)	3251.3(14)	3150.4(11)	1775.8(10)
Z	12	2	4	4	2
T/K	293(2)	293(2)	293(2)	293(2)	293(2)
μ/mm^{-1}	0.077	1.518	1.285	1.301	1.180
No. reflections measured	19,507	29,405	3464	5820	3156
No. unique reflections	6748	5391	2813	4210	2661
R_{int}	0.084	0.046	0.026	0.038	0.089
R_1	0.063	0.031	0.066	0.036	0.076
wR_2	0.157	0.077	0.181	0.090	0.071

SMART-CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using SMART and SAINT programs.[20] Intensities of complexes **2**, **3** and **4** were collected on a Siemens P4 four-circle diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the $\omega - 2\theta$ scan mode. Data were corrected for Lorentz and polarization effects during data reduction using XSCANS[21] and a semi-empirical absorption correction from ψ-scans was applied. The structures were solved by direct methods and refined on F^2 using full-matrix least-squares methods in SHELXTL, version 5.1.[22] Anisotropic thermal parameters were refined for non-hydrogen atoms for both ligands and complexes **1**, **2** and **3**. For complex **4**, the non-hydrogen atoms, except the silver atoms, were refined isotropically, due to the poor quality of the crystals resulting from the rapid loss of lattice solvent molecules. Hydrogen atoms were localized in their calculated positions and refined using a riding model.

CCDC reference numbers 182818 and 182820–182823. See http://www.rsc.org/suppdata/nj/b1/b111661b/ for crystallographic data in CIF or other electronic format.

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References

1 (*a*) C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005; (*b*) E. C. Constable, *Comprehensive Supramolecular Chemistry*, ed. J.-P. Sauvage, Elsevier, Oxford, 1996, vol. 9, pp. 213–252.

2 B. Hasenknopf, J.-M. Lehn, N. Boumediene, A. Dupont-Gervais, A. V. Dorsselaer, B. Kneisel and D. Fenske, *J. Am. Chem. Soc.*, 1997, **119**, 10 956.

3 M. J. Hannon, C. L. Painting, A. Jackson, J. Hamblin and W. Errington, *Chem. Commun.*, 1997, 1807.

4 (*a*) C. J. Fang, C. Y. Duan, C. He and Q. J. Meng, *Chem Commun.*, 2000, 1187; (*b*) C. He, C. Y. Duan, C. J. Fang and Q. J. Meng, *J. Chem. Soc., Dalton Trans.*, 2000, 2419; (*c*) C. J. Fang, C. Y. Duan, H. Mo, C. He, Q. J. Meng, Y. J. Liu, Y. H. Mei and Z. M. Wang, *Organometallics*, 2001, **20**, 2525..

5 (*a*) M. Albrecht and S. Kotila, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2134; (*b*) J. Xu, T. N. Parac and K. N. Raymond, *Angew. Chem., Int. Ed.*, 1999, **38**, 2878; (*c*) B. Kersting, M. Meyer, R. E. Powers and K. N. Raymond, *J. Am. Chem. Soc.*, 1996, **118**, 7221..

6 B. R. Serr, K. A. Andersen, C. M. Elliott and O. P. Anderson, *Inorg. Chem.*, 1988, **27**, 4499.

7 P. K. Bowyer, K. A. Porter, A. D. Rae, A. C. Willis and S. B. Wild, *Chem. Commun.*, 1998, 1153.

8 (*a*) M. J. Hannon, C. L. Painting and N. W. Alcock, *Chem. Commun.*, 1999, 2023; (*b*) M. J. Hannon, S. Bunce, A. J. Clarke and N. W. Alcock, *Angew. Chem., Int. Ed.*, 1999, **38**, 1277..

9 R. Ziessel, A. Harriman, A. El-Ghayoury, L. Douce, E. Leize, H. Nierengarten and A. V. Dorsselaer, *New. J. Chem.*, 2000, **24**, 729.

10 (*a*) W. J. Stratton and D. H. Busch, *J. Am. Chem. Soc.*, 1958, **80**, 3191; (*b*) E. C. Kesslen, W. B. Euler and B. M. Foxman, *Chem. Mater.*, 1999, **11**, 336.

11 L. J. Childs, N. W. Alcock and M. J. Hannon, *Angew. Chem., Int. Ed.*, 2001, **40**, 1079.

12 (*a*) Z. H. Liu, C. Y. Duan, J. Hu and X. Z. You, *Inorg. Chem.*, 1999, **38**, 1719; (*b*) Z. H. Liu, C. Y. Duan, J. H. Li, Y. J. Liu, Y. H. Mei and X. Z. You, *New. J. Chem.*, 2000, **24**, 1057 and references therein..

13 (*a*) C. Y. Duan, Z. H. Liu, X. Z. You, F. Xue and T. C. W. Mak, *Chem. Commun.*, 1997, 381; (*b*) C. He, C. Y. Duan, C. J. Fang, Y. J. Liu and Q. J. Meng, *J. Chem. Soc., Dalton Trans.*, 2000, 1207..

14 (*a*) L. A. Cuccia, J.-M. Lehn, J.-C. Homo and M. Schmutz, *Angew. Chem., Int. Ed.*, 2000, **39**, 233; (*b*) A. Erxleben, *Inorg. Chem.*, 2001, **40**, 412; (*c*) V. Berl, I. Huc, R. G. Khoury and J.-M. Lehn, *Chem. Eur. J.*, 2001, **7**, 2810; (*d*) T. J. Katz, *Angew. Chem., Int. Ed.*, 2000, **39**, 1921; (*e*) A. Erxleben, *Inorg. Chem.*, 2001, **40**, 2928; (*f*) E. Psillakis, J. C. Jeffery, J. A. McCleverty and M. D. Ward, *J. Chem. Soc., Dalton Trans*, 1997, 1645..

15 (*a*) P. K. K. Ho, S. M. Peng, K. Y. Wong and C. M. Che, *J. Chem. Soc., Dalton Trans.*, 1996, 1829; (*b*) C. Piguet, J.-C. G. Bünzli, G. Bernardinelli, G. Hopfgartner, S. Petoud and O. Schaad, *J. Am. Chem. Soc.*, 1996, **118**, 6681..

16 G. Hopfgartner, C. Piguet and J. D. Henion, *J. Am. Soc. Mass Spectrom.*, 1994, **5**, 748.

17 (*a*) T. M. Garrett, U. Koert, J.-M. Lehn, A. Rigault, D. Meyer and J. Fischer, *J. Chem. Soc., Chem. Commun.*, 1990, 557; (*b*) G. C. Van Stein, H. Van der Poel, G. Van Koten, A. L. Spek, A. J. M. Duisenberg and P. S. Pregosin, *J. Chem. Soc. Chem. Commun.*, 1980, 1016; (*c*) G. C. van Stein, G. van Koten, K. Vrieze, C. Brevard and A. L. Spek, *J. Am. Chem. Soc.*, 1984, **106**, 4486..

18 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY, 3rd edn., 1960.

19 (*a*) M. Nishio, *Kagaku No Ryoiki*, 1977, **31**, 998; (*b*) M. Nishio and M. Hirota, *Tetrahedron*, 1989, **45**, 7201; (*c*) M. Nishio, M. Hirota and Y. Umezawa, *The CH/π Interaction, Evidence, Nature and Consequences*, John Wiley & Sons, Inc., New York, 1998..

20 SMART and SAINT. Area Detector Control and Integration Software, Siemens Analytical X-ray Systems, Inc., Madison, WI, USA, 1996.

21 XSCANS, version 2.1, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1994.

22 G. M. Sheldrick, *SHELXTL v5.1 Software Reference Manual*, Bruker AXS, Inc., Madison, WI, USA, 1997.