

Coordination chemistry of bis(2-pyridylimine) ligands with Ag(I): formation of two structurally different coordination polymers and one metallocycle controlled by linker and the solvent system

Harold B. Tanh Jeazet · Jens Mizera ·
Thomas Doert · Kerstin Gloe · Axel Heine ·
Gert Bernhard · Karsten Gloe

Received: 10 June 2011 / Accepted: 22 August 2011 / Published online: 10 September 2011
© Springer Science+Business Media B.V. 2011

Abstract Reaction of equimolar amounts of AgClO_4 and bis[4-(2-pyridylmethyleneamino)phenyl] methane (L^1) or bis[4-(2-pyridylmethyleneamino)phenyl] ether (L^2) in a 1:1 solvent mixture of CH_3CN and CH_2Cl_2 leads to the formation of two infinite coordination polymers of the composition $\{[\text{Ag}(\text{L}^1)]\text{ClO}_4 \cdot \text{CH}_3\text{CN}\}_n$ (**1**) and $\{[\text{Ag}(\text{L}^2)]\text{ClO}_4 \cdot \text{CH}_2\text{Cl}_2\}_n$ (**2**). Whereas **1** represents a homochiral single-stranded helicate the related complex **2** shows a typical zigzag chain arrangement. Both structures are characterized by a distorted tetrahedral coordination environment of the Ag(I) centres each based on a N_4 coordination pattern of two ligand molecules. The resulting strands are connected by a hydrogen bonding network including ClO_4^- anions and solvent molecules forming 2-D layers. Additional π - π and CH - π interactions between the aromatic parts of the ligand molecules give a 3-D arrangement of the packing. In contrast, a discrete dinuclear metallocycle, $[\text{Ag}_2(\text{L}^2)_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{OH}$ (**3**), has been formed by reaction of AgClO_4 with L^2 when CH_2Cl_2 in the solvent mixture was replaced by CH_3OH . Again each Ag(I) has a distorted tetrahedral geometry and is coordinated to two pyridylimine units of two ligand molecules. Additional weak hydrogen bonds involving perchlorate and solvent

molecules as well as edge-to-face and face-to-face π - π interactions allow a 3-D packing arrangement.

Keywords Silver(I) · Bis(2-pyridylimine) ligands · Self-assembly · Supramolecular chemistry

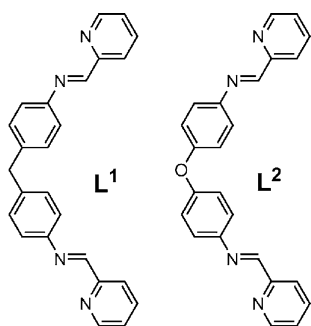
Introduction

The coordination chemistry of multifunctional pyridine ligands has been the focus of a considerable number of investigations. One of the main areas of research relates to the self-assembly of corresponding metal complexes, and gaining an understanding of the factors that affect such processes remains a challenge [1, 2]. Among the ligand types used, the bis(2-pyridylimine) mixed donor system linked directly, or by different spacer units, has been of considerable interest [3–24]. This ligand category was introduced by Yoshida and Ichikawa [4] and Hannon et al. [5] in 1997. The ligands are known for their ability to form coordination polymers [6–8], metallocycles [9, 10] as well as single-, double- and triple-stranded or circular helicates [11–24] with various d -block metal ions. Generally, due to its coordination flexibility allowing the design of manifold supramolecular architectures with useful properties, the d^{10} ion Ag(I) has received increasing attention [25–30]; it has been demonstrated to form a range of different complexes also with structurally related N_4 -donor ligands to those studied in this work [6–13, 15–19, 21, 24]. Hannon et al. found that L^1 forms both a dimeric box-like complex and a double-stranded helicate with Ag(I) in solution [5, 13]. Cheng et al. have succeeded in the characterization of a crystalline dinuclear box-like complex between AgBF_4 and L^2 [9], whereas Tesouro Vallina and Stoeckli-Evans could isolate a coordination polymer with zigzag motif by

Dedicated to Len Lindoy, a remarkable chemist and good friend, on the occasion of his 75th birthday.

H. B. Tanh Jeazet · J. Mizera · T. Doert · K. Gloe ·
A. Heine · K. Gloe (✉)
Department of Chemistry and Food Chemistry,
TU Dresden, 01062 Dresden, Germany
e-mail: karsten.gloe@chemie.tu-dresden.de

H. B. Tanh Jeazet · G. Bernhard
Institute of Radiochemistry, Helmholtz Centre
Dresden-Rossendorf, 01314 Dresden, Germany



Scheme 1 Ligands studied in this work

reaction of L^2 with $\text{Ag}(\text{CF}_3\text{SO}_3)$ [6]. Both groups used similar experimental conditions; the solvent was methanol and the concentration ratio of $\text{Ag}(\text{I})$ to ligand 1:1.

Our interests span ion recognition and binding processes by multifunctional pyridine ligands as well as the build-up of supramolecular assemblies based on both coordinate bonding and weak non-covalent interactions [23, 24, 31–35].

We have employed a series of bis-pyridylimine derivatives having different linking elements as building blocks for new supramolecular architectures [23, 24]. As part of our ongoing studies we report herein results of the self-assembly of the two bis(2-pyridylimine) ligands L^1 and L^2 , having a diphenyl methane or a diphenyl ether linkage (Scheme 1), with silver(I) perchlorate. The architecture of three novel $\text{Ag}(\text{I})$ complexes and the factors influencing the self-assembly process in their formation are discussed.

Experimental

General

All reagents and solvents were purchased from commercial sources and used without further purification. Elemental analysis (C, H, N) were carried out on a Carlo Erba (EA

Table 1 Crystal and structure refinement data for the silver(I) complexes **1**, **2** and **3**

Compound	$\{[\text{Ag}(\text{L}^1)]\text{ClO}_4 \cdot \text{CH}_3\text{CN}\}_n$ (1)	$\{[\text{Ag}(\text{L}^2)]\text{ClO}_4 \cdot \text{CH}_2\text{Cl}_2\}_n$ (2)	$[\text{Ag}_2(\text{L}^2)_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{OH}$ (3)
Molecular formula	$\text{C}_{27}\text{H}_{25}\text{AgClN}_5\text{O}_4$	$\text{C}_{25}\text{H}_{20}\text{AgCl}_3\text{N}_4\text{O}_5$	$\text{C}_{25}\text{H}_{22}\text{Ag}_2\text{Cl}_2\text{N}_4\text{O}_{11}$
Mr	624.82	670.67	1203.53
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1$	$Pbca$	$P-1$
a (Å)	12.065(1)	15.347(7)	9.748(2)
b (Å)	7.984(1)	14.820(5)	10.586(1)
c (Å)	14.182(1)	23.269(2)	12.722(3)
α (°)	90	90	85.28(1)
β (°)	103.96(1)	90	75.77(2)
γ (°)	90	90	85.55(1)
V (Å ³)	1325.9(1)	5292(3)	1266.0(4)
D_c (g cm ⁻³)	1.57	1.68	1.58
Z	2	8	1
Crystal size (mm ³)	0.50 × 0.08 × 0.04	0.25 × 0.10 × 0.10	0.30 × 0.24 × 0.14
Crystal colour	Yellow	Pale yellow	Pale yellow
Crystal habit	Needle	Needle	Needle
Temperature (K)	200(2)	198(2)	198(2)
λ (MoK α)	0.71073	0.71073	0.71073
μ (MoK α) (mm ⁻¹)	0.90	1.11	0.95
$2\theta_{\text{max}}$ (°)	60.0	50.8	56.0
N	12321	68399	48498
N_{ind} (R_{merge})	6922 (0.023)	4858 (0.061)	6028 (0.078)
N_{obs} —($I > 2\sigma(I)$)	6125	3544	3965
$R1^a$ —($I > 2\sigma(I)$)	0.037	0.044	0.058
$wR2^a$ —(all)	0.097	0.098	0.138
Residual Extr. (e ⁻ Å ⁻³)	0.82 (-0.40)	0.61 (-0.71)	1.23 (-0.54)

^a $R1 = \sum |F_o| - |F_c| / \sum |F_o|$ for $F_o > 2r(F_o)$ and $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_c^2)^2]\}^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$, $P = (F_o^2 + 2F_c^2)/3$ and A and B are listed in the crystal data information supplied

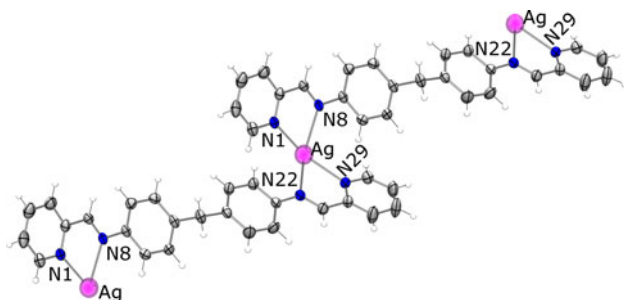


Fig. 1 ORTEP representation of the local coordination environment of Ag(I) in **1**; Atoms are represented as 50% thermal ellipsoids. Anions and solvent molecules are omitted for clarity

Table 2 Selected bond lengths (Å) and angles (°) for $\{[Ag(L^1)]ClO_4 \cdot CH_3CN\}_n$ (**1**)

Bond lengths (Å)	
Ag–N ₁	2.412(3)
Ag–N ₈	2.302(3)
Ag–N ₂₂	2.458(3)
Ag–N ₂₉	2.254(2)
Bond angles (°)	
N ₁ –Ag–N ₈	72.39(9)
N ₁ –Ag–N ₂₂	105.70(8)
N ₁ –Ag–N ₂₉	148.72(11)
N ₈ –Ag–N ₂₂	126.37(9)
N ₈ –Ag–N ₂₉	134.86(9)
N ₂₂ –Ag–N ₂₉	72.30(9)

1108) Analyser. ¹H NMR spectra were recorded on Bruker Avance DRX-500 spectrometer at 500 MHz, and electrospray ionisation mass spectra (ESI-MS) were obtained on a Finnigan LCQ spectrometer using methanol as mobile phase.

Ligand synthesis

Ligands L¹ and L² were prepared using the literature procedure [5, 9]. Characterization data were in agreement with those reported previously [9, 22].

Complex synthesis

Caution: Perchlorate complexes are potentially explosive and appropriate caution should be exercised in their synthesis and handling.

$\{[Ag(L^1)]ClO_4 \cdot CH_3CN\}_n$ (**1**) and $\{[Ag(L^2)]ClO_4 \cdot CH_2Cl_2\}_n$ (**2**)

Silver perchlorate (11.0 mg, 0.05 mmol) in acetonitrile (1 mL) was added to L¹ or L² (20.0 mg, 0.05 mmol) in dichloromethane (1 mL). Yellow needles of the complexes were obtained by slow diffusion of diethyl ether into the

Table 3 C–H···O, C–H···N and C–H···Cg interactions in the complexes **1**, **2** and **3**

C–H	A	H···A [Å]	C···A [Å]	C–H···A [°]
$\{[Ag(L^1)]ClO_4 \cdot CH_3CN\}_n$ (1)				
C7–H7	O2A	2.43	3.41	159
C14–H14	O2A	2.62	3.62	171
C15–H15A	O4A	2.37	3.31	159
C20–H20	N1	2.60	3.52	163
C24–H24	N31	2.62	3.55	164
C25–H25	O3A	2.34	3.11	134
C27–H27	O1A	2.48	3.36	154
C4–H4	O2A	2.64	3.36	133
C20–H20	Cg4	2.91	3.80	156
C18–H18	Cg6	3.12	3.83	133
C17–H17	Cg7	2.97	3.90	168
$\{[Ag(L^2)]ClO_4 \cdot CH_2Cl_2\}_n$ (2)				
C3–H3	O3	2.62	3.55	164
C30A–H30A	O4	2.47	3.44	168
C30A–H30A	O1	2.82	3.64	139
C30A–H30B	O3	2.57	3.33	134
C10–H10	O4	2.71	3.58	151
C7–H7	O1	2.68	3.46	139
C20–H20	O2	2.71	3.41	131
C13–H13	Cg4	3.09	3.96	153
C21–H21	Cg5	2.82	3.58	138
C26–H26	Cg6	2.60	3.54	169
C2–H2	Cg7	2.96	3.90	173
$[Ag_2(L^2)_2](ClO_4)_2 \cdot CH_3OH$ (3)				
O1M–H1M	O3A	1.72	2.60	161
C14–H14	O4A	2.51	3.46	178
C23–H23	O3A	2.51	3.43	163
C28–H28	O1M	2.63	3.32	130
C3–H3	O4A	2.65	3.58	168
C10–H10	O3A	3.06	4.01	178
C11–H11	Cg5	2.88	3.80	163
C20–H20	Cg6	2.93	3.78	149
C4–H4	Cg7	3.55	4.48	166

Table 4 Selected bond lengths (Å) and angles (°) for the complex $\{[Ag(L^2)]ClO_4 \cdot CH_2Cl_2\}_n$ (**2**)

Bond lengths (Å)	
Ag–N ₁	2.260(3)
Ag–N ₈	2.373(3)
Ag–N ₂₂	2.395(3)
Ag–N ₂₅	2.252(3)
Bond angles (°)	
N ₁ –Ag–N ₈	72.76(12)
N ₁ –Ag–N ₂₂	139.62(12)
N ₁ –Ag–N ₂₅	134.08(12)
N ₈ –Ag–N ₂₂	110.66(11)
N ₈ –Ag–N ₂₅	135.96(12)
N ₂₂ –Ag–N ₂₅	72.63(11)

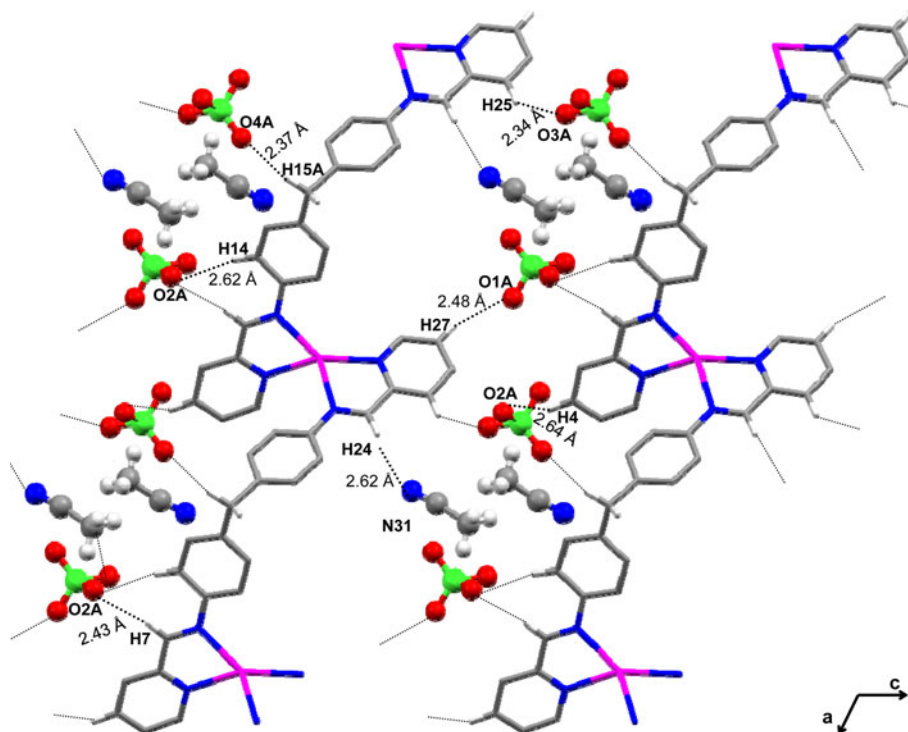
Table 5 Selected bond lengths (Å) and angles (°) for complex $[\text{Ag}_2(\text{L}^2)_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{OH}$ (**3**)

Bond lengths (Å)	
Ag–N ₁	2.424(4)
Ag–N ₈	2.308(4)
Ag–N ₂₂	2.430(3)
Ag–N ₂₉	2.293(4)
Bond angles (°)	
N ₁ –Ag–N ₈	71.08(13)
N ₁ –Ag–N ₂₂	132.02(13)
N ₁ –Ag–N ₂₉	115.47(14)
N ₈ –Ag–N ₂₂	117.69(12)
N ₈ –Ag–N ₂₉	162.14(13)
N ₂₂ –Ag–N ₂₉	71.40(13)

resulting solution in the dark over 2–3 days. The crystals were collected, washed with ether, and dried under vacuum.

1: Yield, 17 mg (55%) Found: C, 51.29%, H, 3.23%, N, 9.59%. Cal. for $[\text{Ag}(\text{C}_{25}\text{H}_{20}\text{N}_4)]\text{ClO}_4$ (583.77); C, 51.44%, H, 3.45%, N, 9.60%. MS (ESI) m/z : 1067, $[\text{Ag}_2\text{L}_2 + \text{ClO}_4]^+$; 690, $[\text{Ag}_2\text{L} + \text{ClO}_4]^+$; 861, $[\text{AgL}_2]^+$; 485, $[\text{Ag}_2\text{L}_2]^{2+}$.

2: Yield, 27 mg (87%) Found: C, 48.68%, H, 2.53%, N, 9.38%. Cal. for $[\text{Ag}(\text{C}_{24}\text{H}_{18}\text{N}_4\text{O})]\text{ClO}_4$ (585.74); C, 49.21%, H, 3.10%, N, 9.57%. MS (ESI) m/z : 863, $[\text{AgL}_2]^+$; 485, $[\text{Ag}_2\text{L}_2]^{2+}$.

Fig. 2 2-D Arrangement of the mono-helical strands of complex **1** based on hydrogen bonding network including perchlorate/acetonitrile pairs. Hydrogen atoms without H bond connection are omitted for clarity $[\text{Ag}_2(\text{L}^2)_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{OH}$ (**3**)

Silver perchlorate (11.0 mg, 0.05 mmol) in acetonitrile (1 mL) was added to L^2 (20.0 mg, 0.05 mmol) in a mixture of methanol/acetonitrile (1:1) (1 mL). Pale yellow needles of the complex were obtained by slow diffusion of diethyl ether into the resulting solution in the dark over 3 days. The crystals were collected, washed with ether, and dried under vacuum.

3: Yield, 19 mg (61%) Found: C, 48.89%, H, 2.80%, N, 9.51%. Cal. for $[\text{Ag}_2(\text{C}_{24}\text{H}_{18}\text{N}_4\text{O})_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{OH}$ (1203.53); C, 48.90%, H, 3.35%, N, 9.31%. MS (ESI) m/z : 1167, $[\text{Ag}_2\text{L}_2 + (\text{ClO}_4)_2 - \text{H}]^-$; 610, $[\text{AgLOAc} + 2\text{MeOH} + \text{H}]^+$; and 485, $[\text{Ag}_2\text{L}_2]^{2+}$.

X-Ray structure determinations

Crystals employed for the X-ray determinations were obtained directly from the respective reaction solutions and were used without further drying. Intensities were collected on a Nonius Kappa CCD or a Kappa Apex II CCD diffractometer with ω and ψ scans to approximately 50° 2θ at 198(2) or 200(2) K, both using graphite-monochromated Mo-K α radiation generated from a sealed tube (0.71073 Å). The following programs were used for data collection, integration and data reduction: COLLECT [36], Dirax/lsq [37], EvalCCD [38], Apex Suite [39]. Multi-scan empirical

Fig. 3 Crystal packing of **1** showing the π - π interactions between the single helical strands. Hydrogen atoms are omitted for clarity

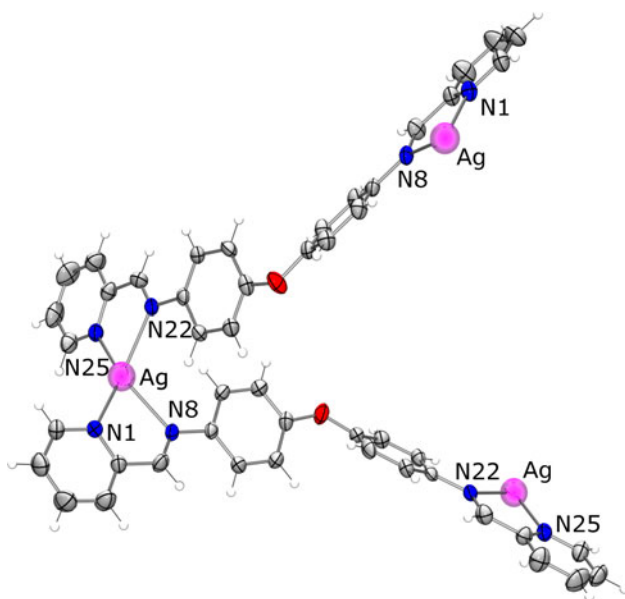
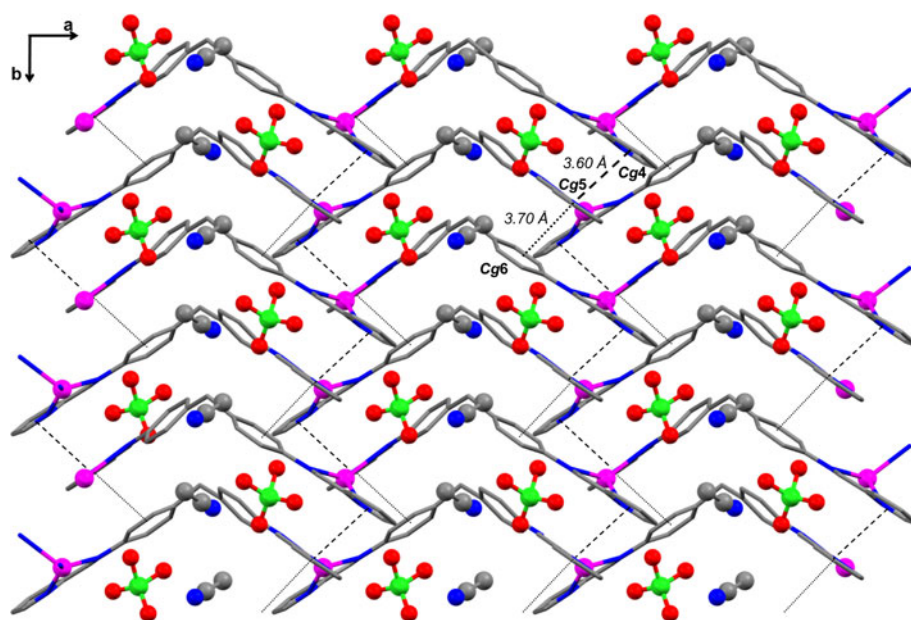


Fig. 4 ORTEP diagram of the molecular structure of complex **2**. Thermal ellipsoids are shown at the 50% probability level

absorption corrections were applied to all data sets using the program SADABS [40]. The structures were solved by direct methods with the programs SIR97 [41] or SHELXS-97 [42]. All structures were refined and extended with SHELXL-97 [43]. In general, ordered non-hydrogen atoms with occupancies greater than or equal to 0.5 were refined anisotropically. Partial occupancy carbon, nitrogen and oxygen atoms were refined isotropically. Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. Oxygen-bound hydrogen atoms that were structurally evident in the difference

Fourier map were included and refined with bond length and angle restraints. Parameters for data collection and structure refinement data for all structures are summarised in Table 1. ORTEP [44] depictions of the three complex structures are given in Figs. 1, 4 and 7, selected bond lengths and angles in Tables 2, 3, 4, 5.

Results and discussion

Structure of $\{[Ag(L^1)ClO_4 \cdot CH_3CN]\}_n$ (**1**)

The reaction of L^1 with equimolar amounts of $AgClO_4$ in a 1:1 solvent mixture of CH_3CN and CH_2Cl_2 results in the formation of the coordination polymer **1** having a monohelical arrangement. As shown in Fig. 1 and Table 2, each $Ag(I)$ is coordinated by two chelating pyridylimine units of two ligands giving a distorted tetrahedral coordination geometry. All bond lengths and angles are within the expected ranges, but the different lengths of both $Ag-N_{pyridyl}$ ($Ag-N1$: 2.412 Å, $Ag-N29$: 2.254 Å) and $Ag-N_{imine}$ ($Ag-N8$: 2.302 Å, $Ag-N22$: 2.458 Å) bonds are a precondition for twisting the molecule.

In addition the two pyridylimine arms within the ligand molecule are not planar and the diphenyl methane linker shows a strong twist around the central methylene of about 107° leading to opposite directed pyridylimine donor functions and generating helical strands along a -axis. The crystal studied was homochiral and possesses a right-handed (P) orientation of the helix. Single helical strands are connected within the ac -plane by an extensive hydrogen bonding network including pairs of one ClO_4^- ion and one

Fig. 5 Side view along the *b*-axis of **2** showing the layers formed by hydrogen bonding network including perchlorate anions and CH₂Cl₂ molecules and chlorine- π contacts. Non-involved hydrogen atoms are omitted for clarity

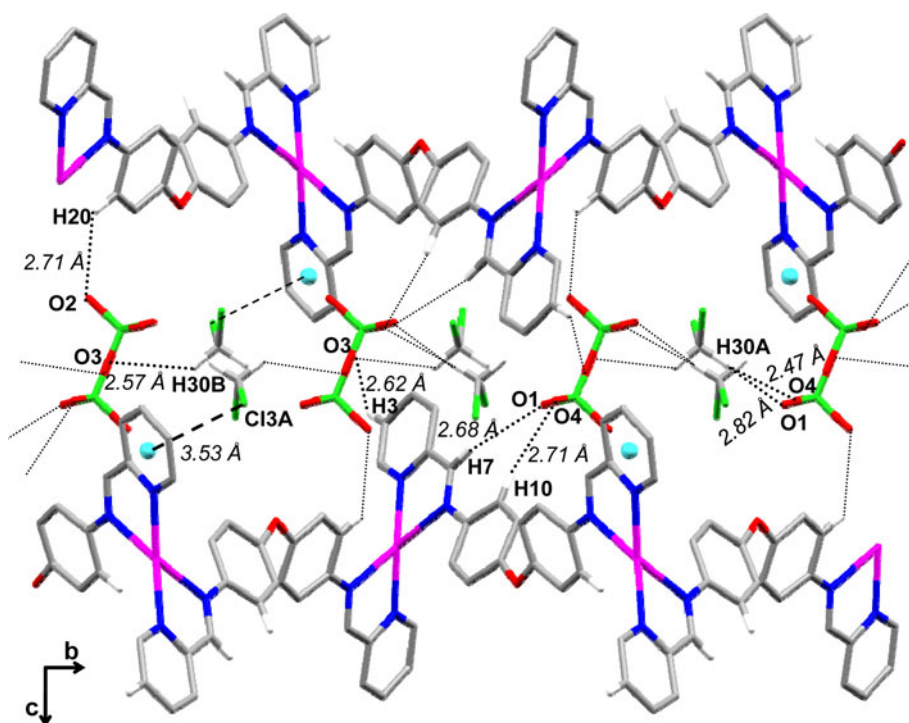
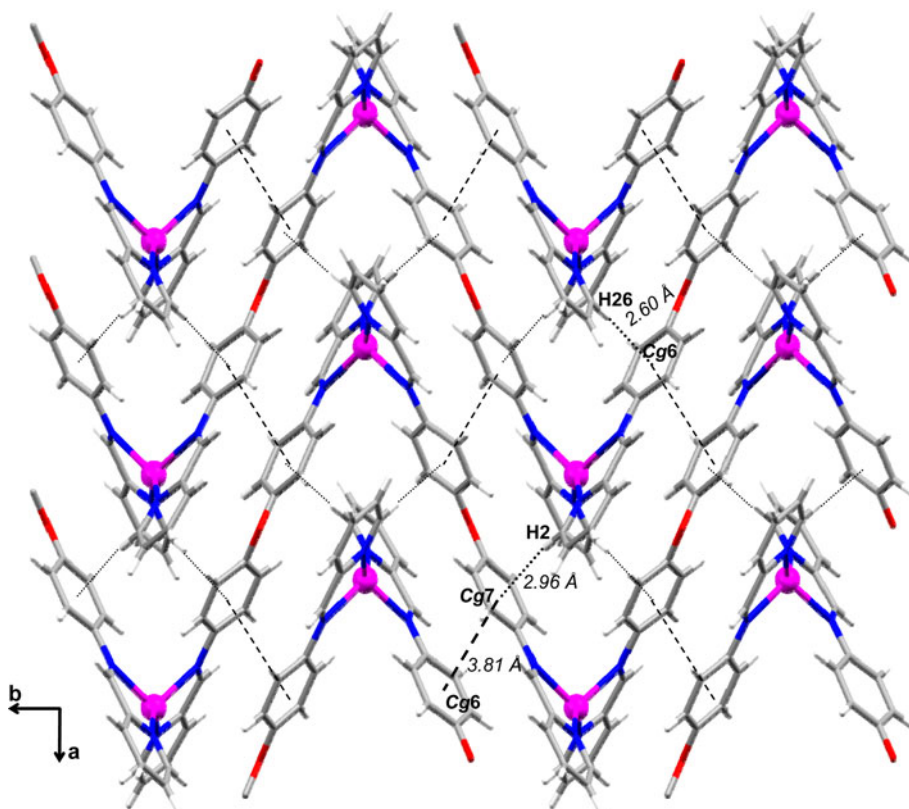


Fig. 6 Crystal packing of **2** showing the typical zigzag arrangement and the π - π stacking and CH- π interactions between adjacent chains. Perchlorate anions and dichloromethane molecules are omitted for clarity



CH₃CN solvent molecule (Fig. 2, Table 3). As a result two-dimensional layers are formed.

The crystal packing is stabilized by additional π - π stacking interactions (Fig. 3) between phenyl and pyridyl

units ($Cg6 \cdots Cg5$ distance 3.70 Å; $\beta = 18^\circ$) as well as pyridyl rings themselves ($Cg5 \cdots Cg4$ distance 3.60 Å; $\beta = 19^\circ$) and CH- π interactions (Table 3) between adjacent phenyl rings (C-H \cdots Cg distances 2.91–3.12 Å). This

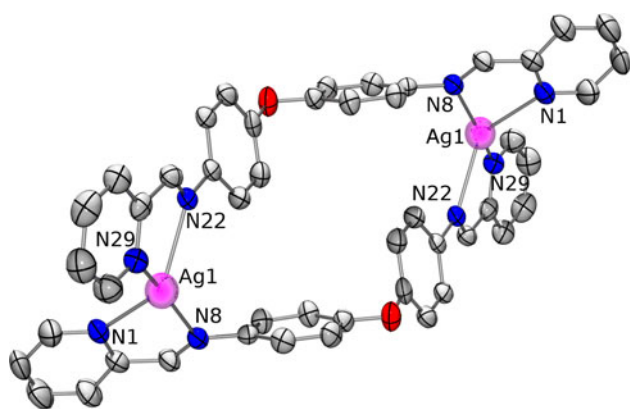


Fig. 7 ORTEP plot of the cyclic $[\text{Ag}_2(\text{L}^2)_2]^{2+}$ cation showing 50% probability displacement ellipsoids. Hydrogen atoms, perchlorate anions and CH_3OH molecules are omitted for clarity

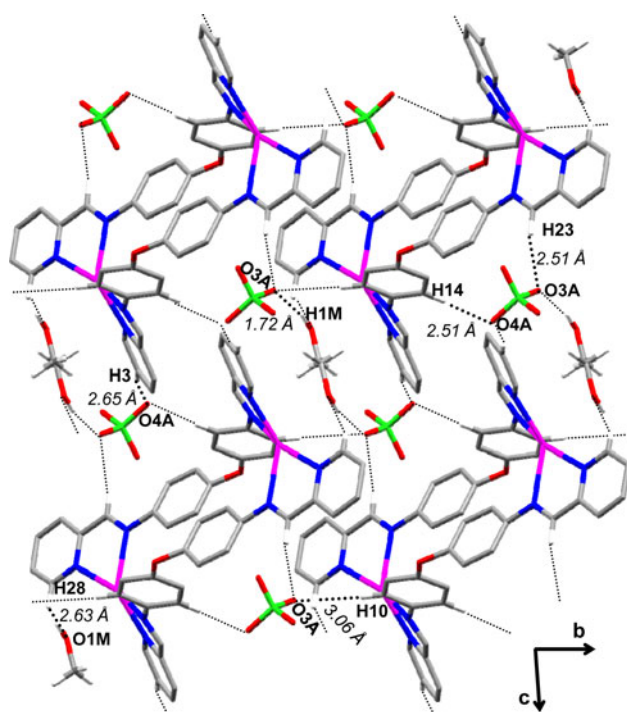


Fig. 8 Hydrogen bonding network within the structure **3** showing the interactions between ClO_4^- and one disordered CH_3OH molecule with adjacent phenyl and pyridyl units and leading to 2-D layers. Non-interacting Hydrogen atoms are omitted for clarity

combination of different weak interactions within complex **1** should be an important factor of influence in favouring the helical twist of the polymeric chains formed.

Structure of $\{[\text{Ag}(\text{L}^2)]\text{ClO}_4 \cdot \text{CH}_2\text{Cl}_2\}_n$ (**2**)

Under identical experimental conditions as for ligand L^1 the reaction of L^2 with AgClO_4 also gives a coordination polymer with a related composition of $\{[\text{Ag}(\text{L}^2)]\text{ClO}_4 \cdot \text{CH}_2\text{Cl}_2\}_n$ (**2**); again the typical N_4 coordination

environment of each $\text{Ag}(\text{I})$ centre is formed by two ligand molecules (Fig. 4). Also the bond lengths and angles are in the same order of magnitude (Table 4). However, both phenyl rings of the linker are twisted with respect to each other by only 52° and the ligand arms are, in contrast to **1**, almost planar; the angles with respect to pyridyl-phenyl planes are 6° and 10° . The result is a distinct change of the crystal packing as shown in Figs. 5 and 6.

In contrast to the helicate **1**, complex **2** forms polymeric zigzag chains which are connected to 2D-layers by an extended hydrogen bonding network that includes the ClO_4^- anions and CH_2Cl_2 molecules (Fig. 5, Table 3). These layers are stabilized by additional rare $\text{C}-\text{Cl} \cdots \pi$ contacts of the solvent CH_2Cl_2 with the pyridyl units ($\text{C}-\text{Cl} \cdots \text{Cg}$ distance 3.53 Å) and weak $\text{CH} \cdots \text{O}$ contacts (2.57 Å) between anions and solvent molecules.

The two-dimensional layers are stabilized by $\text{CH}-\pi$ interactions (Fig. 6, Table 3) as well as $\pi-\pi$ interactions ($\text{Cg}-\text{Cg}$ distance 3.81 Å; $\beta = 27^\circ$) along the *c*-axis.

The structure of complex **2** corresponds to a large extent with the previously reported $\text{Ag}(\text{I})$ complex by Tesouro Vallina and Stoeckli-Evans having the composition $\{[\text{Ag}(\text{L}^2)]\text{CF}_3\text{SO}_3 \cdot 0.4\text{H}_2\text{O}\}_n$ [**6**].

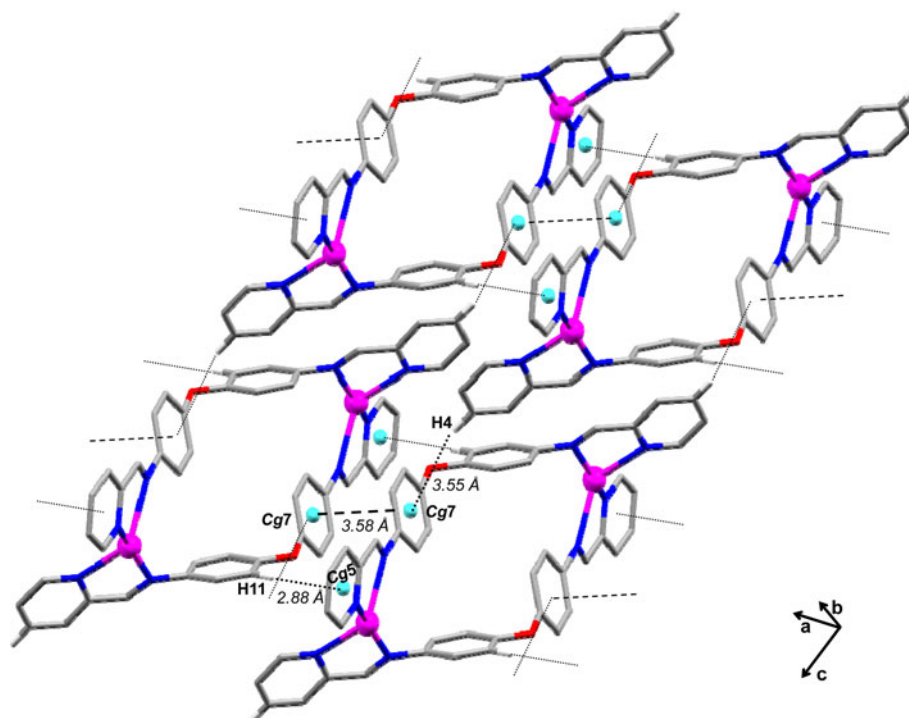
Structure of $[\text{Ag}_2(\text{L}^2)_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{OH}$ (**3**)

In the case of L^2 a second $\text{Ag}(\text{I})$ complex of composition $[\text{Ag}_2(\text{L}^2)_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{OH}$ (**3**) has been isolated. In contrast to the experiments leading to coordination polymers, in this preparation the CH_2Cl_2 in the solvent mixture was replaced by CH_3OH . The molecular structure of the complex shown in Fig. 7 is characterized by a cyclic arrangement that is closely related to the $\text{Ag}(\text{I})$ complex of composition $[\text{Ag}_2(\text{L}^2)_2](\text{BF}_4)_2 \cdot 1.5\text{CH}_3\text{CN}$ described by Cheng et al. [**9**].

Again both silver (I) ions are coordinated by two pyridylimine arms of the two different ligand molecules giving distorted tetrahedral coordination geometries. However, in contrast to the polymers discussed above, a discrete metallocycle is formed. Each ligand bridges both $\text{Ag}(\text{I})$ centres; one ligand molecule passes above the $\text{Ag}(\text{I})-\text{Ag}(\text{I})$ axis and the other beneath. Such an arrangement is much more twisted than occurs in the polymer structures. The torsion angle of the two central phenyl rings around the ether oxygen linker is 77° , between the related angles in **1** and **2**. In contrast, one of the pyridylimine arms is twisted with a pyridyl-phenyl angle of 56° while the second is only moderately twisted with an angle of 19° .

In analogy to **1** and the related literature example [**9**] the observed lengths of the $\text{Ag}-\text{N}_{\text{pyridyl}}$ or $\text{Ag}-\text{N}_{\text{imine}}$ bonds differ by around 0.13 Å each (Table 5). The metallocycles are connected by hydrogen bonding interactions including perchlorate anions and methanol solvent molecules

Fig. 9 3-D packing arrangement of complex **3** based on π - π stacking and CH- π interactions. Hydrogen atoms not involved in binding, perchlorate anions and CH₃OH molecules are omitted for clarity



forming 2-D layers in the *bc*-plane (Fig. 8, Table 3). Due to an occupational disorder of the solvent (a site occupancy of 0.5 is observed in the refinement), methanol molecules are statistically present in every second void only.

Strong intermolecular face-to-face π - π interactions between the phenyl rings (Cg7-Cg7 distance 3.58 Å; $\beta = 22^\circ$) along the *a*-axis and CH- π interactions (CH...Cg5 2.88 Å; angle 163°) along *c*-axis result in a 3-D packing arrangement (Fig. 9).

Conclusions

In this study three different supramolecular silver(I) perchlorate complexes of two structure-related bis(pyridylimine) ligands (L^1 and L^2) have been successfully synthesized and their structures characterized by X-ray structure analysis. The observed structural motifs shown in Fig. 10 correspond to the known coordination patterns of this ligand type toward Ag(I) [6, 9, 11].

Two kinds of coordination polymers, a single-stranded homochiral helicate **1** and a zigzag-chain arrangement **2**, resulting from the two ligands possessing slightly different linking elements for the pyridylimine arms (CH₂ in L^1 against O in L^2) could be identified. The third complex **3** represents a cyclic arrangement connecting two silver ions by two ligand molecules of L^2 . Obviously the formation of the latter one is favoured by replacement of dichloromethane by methanol in the binary solvent mixture used for the reaction. The structural differences within the novel

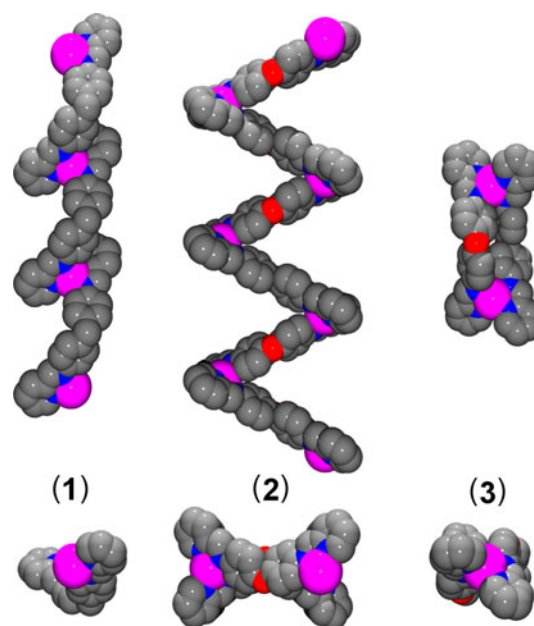


Fig. 10 Structural motifs of Ag(I) complexes with the bis(pyridylimine) ligands studied in this work: side and top view of the right-handed (P) homochiral single-stranded helicate **1**, the coordination polymer of zigzag chain type **2** and the discrete metallocycle **3**

three complexes and the related examples in literature [6, 9, 11] clearly illustrate the significance of both the kind of the linker as well as the nature of the counter anion and the solvent system for the sensitive interplay of weak interactions during the self-assembly process. However, the

overall rationale for the different performance observed remains unclear.

Supplementary material

CCDC 828802 (**1**), 828803 (**2**) and 828804 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/datarequest/cif, or by emailing data request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Acknowledgments Financial support of this work by the German Federal Ministry of Education and Research (BMBF-project 02NUK014A) and the European Social Fund (ESF) is gratefully acknowledged.

References

1. Glasson, C.R.K., Lindoy, L.F., Meehan, G.V.: Recent developments in the d-block metallo-supramolecular chemistry of polypyridyls. *Coord. Chem. Rev.* **252**, 940–963 (2008)
2. Steel, P.J.: Ligand design in multimetallic architectures: six lessons learned. *Acc. Chem. Res.* **38**, 243–250 (2005)
3. Hannon, M.J., Childs, L.J.: Helices and helicates: beautiful supramolecular motifs with emerging applications. *Supramol. Chem.* **16**, 7–22 (2004)
4. Yoshida, N., Ichikawa, K.: Synthesis and structure of a dinuclear zinc(II) triple helix of an *N,N*-bidentate Schiff base: new building blocks for the construction of helical structures. *Chem. Commun.* 1091–1092 (1997)
5. Hannon, M.J., Painting, C.L., Jackson, A., Hamblin, J., Errington, W.: An inexpensive approach to supramolecular architecture. *Chem. Commun.* 1807–1808 (1997)
6. Tesouro Vallina, A., Stoeckli-Evans, H.: Catena-poly[silver(I)- μ -{bis[4-(2-pyridylmethyleneamino)phenyl]ether}] trifluoromethanesulfonate 0.4-hydrate: a zigzag coordination polymer. *Acta Crystallogr.* **E57**, m59–m61 (2001)
7. Halder, P., Zangrando, E., Paine, T.K.: Self-assembly of silver(I) and bis-bidentate *N,N*-donor ligands: from a tetranuclear complex to coordination polymers. *Dalton Trans.* 5386–5394 (2009)
8. Chakraborty, B., Halder, P., Paine, T.K.: Conformational supramolecular isomerism in one-dimensional silver(I) coordination polymer of a flexible bis(bidentate) *N,N*-donor ligand with *p*-xylyl spacer. *Dalton Trans.* **40**, 3647–3654 (2011)
9. Cheng, H., Chun-Ying, D., Chen-Jie, F., Qing-Jin, M.: Self-assembled dinuclear molecular box $[\text{Ag}_2\text{L}_2]^{2+}$ and triple helicates $[\text{Co}_2\text{L}_3]^{4+}$, $[\text{Ni}_2\text{L}_3]^{4+}$ {L=bis[4-(pyridylmethyleneamino)phenyl] ether}. *J. Chem. Soc. Dalton Trans.* 2419–2424 (2000)
10. Pascu, M., Clarkson, G.J., Kariuki, B.M., Hannon, M.J.: Aggregation of imine-based metallo-supramolecular architectures through π - π interactions. *Dalton Trans.* 2635–2642 (2006)
11. Bowyer, P.K., Porter, K.A., Rae, A.D., Willis, A.C., Wild, S.B.: From helicate to infinite coordination polymer: crystal and molecular structures of silver(I) complexes of readily prepared di-Schiff bases. *Chem. Commun.* 1153–1154 (1998)
12. Hannon, M.J., Bunce, S., Clarke, A.J., Alcock, N.W.: Spacer control of directionality in supramolecular helicates using an inexpensive approach. *Angew. Chem. Int. Ed.* **38**, 1277–1278 (1999)
13. Hannon, M.J., Painting, C.L., Alcock, N.W.: A metallo-supramolecular double-helix containing a major and a minor groove. *Chem. Commun.* 2023–2024 (1999)
14. Childs, L.J., Alcock, N.W., Hannon, M.J.: Assembly of nanoscale circular supramolecular arrays through π - π aggregation of arc-shaped helicate units. *Angew. Chem.* **113**, 1113–1115 (2001)
15. Tesouro Vallina, A., Stoeckli-Evans, H.: Coordination chemistry of a new imine-ether ligand, *N,N'*-bis(2-pyridylmethylene)-2,2'-(ethylenedioxy)bis(ethylamine): mono-helical and single-helical-strand coordination modes identified by X-ray crystallography. *Polyhedron* **21**, 1177–1187 (2002)
16. Dong, G., Chun-Ying, D., Chun-Qi, Q., Qing-Jin, M.: The synthesis and structural characterisation of helical silver(I) complexes with short bis(pyridylimine) ligands. *New J. Chem.* **26**, 796–802 (2002)
17. Tuna, F., Hamblin, J., Jackson, A., Clarkson, G., Alcock, N.W., Hannon, M.J.: Metallo-supramolecular libraries: triangles, polymers and double-helicates assembled by copper(I) coordination to directly linked bis-pyridylimine ligands. *Dalton Trans.* 2141–2148 (2003)
18. Sun, W.-H., Zhang, T., Wang, L., Chen, Y., Froehlich, R.: Supramolecular helical architecture assembled by double-helical $[\text{Ag}_2\text{L}_2]$ units. *J. Organomet. Chem.* **689**, 43–49 (2004)
19. Childs, L.J., Pascu, M., Clarke, A.J., Alcock, N.W., Hannon, M.J.: Using noncovalent intra-strand and inter-strand interactions to prescribe helix formation within a metallo-supramolecular system. *Chem. Eur. J.* **10**, 4291–4300 (2004)
20. Hamblin, J., Tuna, F., Bunce, S., Childs, L.J., Jackson, A., Errington, W., Alcock, N.W., Nierengarten, H., van Dorsselaer, A., Leize-Wagner, E., Hannon, M.J.: Supramolecular circular helicates formed by destabilisation of supramolecular dimers. *Chem. Eur. J.* **13**, 9286–9296 (2007)
21. Zi, G., Xiang, L., Zhang, Y., Wang, Q., Li, X., Yang, Y., Zhang, Z.: Synthesis and X-ray structures of new chiral Ag(I) complexes with biaryl-based N_4 -donor ligands. *J. Organomet. Chem.* **692**, 3949–3956 (2007)
22. Dehghanpour, S., Lipkowski, J., Mahmoudi, A., Khalaj, M.: Synthesis, spectral characterization and structure of dinuclear double-helical mercury complex containing bis[4-(2-pyridylmethyleneamino)phenyl]-methane ligand. *Polyhedron* **29**, 2802–2806 (2010)
23. Tanh Jeazet, H.B., Gloe, K., Doert, T., Kataeva, O., Jäger, A., Geipel, G., Bernhard, G., Büchner, B., Gloe, K.: Self-assembly of neutral hexanuclear circular copper(II) meso-helicates: topological control by sulfate ions. *Chem. Commun.* **46**, 2373–2375 (2010)
24. Gloe, K., Tanh Jeazet, H.B., Gloe, K., Doert, T., Kataeva, O.N., Bernhard, G.: Coordination behaviour of bis-pyridylimine ligands: polymers, metallamacrocycles and helicates, Program book, 39th ICCG, Adelaide/Australia, 25–30 July, abstract 017 (2010)
25. Khlbystov, A.N., Blake, A.J., Champness, N.R., Lemenovskii, D.A., Majouga, A.G., Zyk, N.V., Schröder, M.: Supramolecular design of one-dimensional coordination polymers based on silver(I) complexes of aromatic nitrogen-donor ligands. *Coord. Chem. Rev.* **222**, 155–192 (2001)
26. Constable, E.C.: Silver coordination polymers-from simple complexes to functional networks. *Aust. J. Chem.* **59**, 1–2 (2006)
27. Chen, C.-L., Kang, B.-S., Su, C.-Y.: Recent advances in supramolecular design and assembly of silver(I) coordination polymers. *Aust. J. Chem.* **59**, 3–18 (2006)
28. Oh, M., Stern, C.L., Mirkin, C.A.: Coordination polymers from silver(I) and bifunctional pyridyl ligands. *Inorg. Chem.* **44**, 2647–2653 (2005)

29. Feazell, R.P., Carson, C.E., Klausmeyer, K.K.: Variability in the structures of [4-(aminomethyl)pyridine]silver(I) complexes through effects of ligand ratio, anion, hydrogen bonding and π -stacking. *Inorg. Chem.* **45**, 935–944 (2006)
30. Slenters, T.V., Sague, J.L., Brunetto, P.S., Zuber, S., Fleury, A., Mirolo, L., Robin, A.Y., Meuwly, M., Gordon, O., Landmann, R., Daniels, A.U., Fromm, K.M.: Of chains and rings: synthetic and theoretical investigations for tuning the structure of silver coordination compounds and their applications. *Materials* **3**, 3407–3429 (2010)
31. Antonioli, B., Bray, D.J., Clegg, J.K., Gloe, K., Gloe, K., Kataeva, O., Lindoy, L.F., McMurtrie, J.C., Steel, P.J., Sumbly, C.J., Wenzel, M.: Silver(I) complexation of linked 2,2'-dipyridylamine derivatives. Synthetic, solvent extraction, membrane transport and X-ray structural studies. *Dalton Trans.* 4783–4794 (2006)
32. Antonioli, B., Bray, D.J., Clegg, J.K., Gloe, K., Gloe, K., Jolliffe, K.A., Jäger, A., Kataeva, O., Lindoy, L.F., Steel, P.J., Sumbly, C.J., Wenzel, M.: Interaction of copper(II) and palladium(II) with linked 2,2'-dipyridylamine derivatives: synthetic and structural studies. *Polyhedron* **27**, 2889–2898 (2008)
33. Antonioli, B., Büchner, B., Clegg, J.K., Gloe, K., Gloe, K., Götzke, L., Heine, A., Jäger, A., Jolliffe, K.A., Kataeva, O., Kataev, V., Klingeler, R., Krause, T., Lindoy, L.F., Popa, A., Seichter, W., Wenzel, M.: Interaction of an extended series of N-substituted di(2-picoly)amine derivatives with copper(II). Synthetic, structural, magnetic and solution studies. *Dalton Trans.* 4795–4805 (2009)
34. Wenzel, M., Wichmann, K., Gloe, K., Gloe, K., Buschmann, H.-J., Otho, K., Schröder, M., Blake, A.J., Wilson, C., Mills, A.M., Lindoy, L.F., Plieger, P.G.: Interaction of tripodal Schiff-base ligands with silver(I): structural and solution studies. *CrystEng-Comm* **12**, 4176–4183 (2010)
35. Götzke, L., Gloe, K., Jolliffe, K.A., Lindoy, L.F., Heine, A., Doert, T., Jäger, A., Gloe, K.: Nickel(II) and zinc(II) complexes of N-substituted di(2-picoly)amine derivatives: synthetic and structural studies. *Polyhedron* **30**, 708–714 (2011)
36. Nonius BV, Delft, The Netherlands, 1998
37. Duisenberg, A.J.M.: Indexing in single-crystal diffractometry with an obstinate list of reflections. *J. Appl. Crystallogr.* **25**, 92–96 (1992)
38. Duisenberg, A.J.M., Kroon-Batenburg, L.M.J., Schreurs, A.M.M.: An intensity evaluation method: EVAL-14. *J. Appl. Crystallogr.* **36**, 220–229 (2003)
39. APEX2 Suite, Kappa Apex II Software Package, Bruker-AXS, Madison, WI (2009)
40. Sheldrick, G.M.: SADABS: Empirical absorption and correction software. University of Göttingen, Germany (1999–2008)
41. Altomare, A., Burla, M.C., Camalli, M., Casciaro, G.L., Giacovazzo, C., Guagliardi, A., Moliterni, A.G.C., Polidori, G., Spagna, R.: SIR97: a new tool for crystal structure determination and refinement. *J. Appl. Crystallogr.* **32**, 115–119 (1999)
42. Sheldrick, G.M.: Phase annealing in SHELX-90—direct methods for larger structures. *Acta Crystallogr. A* **46**, 467–473 (1990)
43. Sheldrick, G.M.: SHELXL-97: programs for crystal structure analysis. University of Göttingen, Germany (1997)
44. Farrugia, L.J.: ORTEP-3 for Windows—a version of ORTEP-III with a Graphical User Interface (GUI). *J. Appl. Crystallogr.* **30**, 565 (1997)