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Construction of co-ordination networks of 1,6-bis(4′-pyridyl)-2,5-diazahexane with silver(I) and copper(I). Structural diversity through change in metal ions and counter ions

Bao-Li Fei,[a] **Wei-Yin Sun,***[a] **Kai-Bei Yu**[b] **and Wen-Xia Tang**[a]

[a] *Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China. E-mail: sunwy@netra.nju.edu.cn*
[b] *Analysis Center, Chengdu Branch of Chinese Academy of Science, Chengdu 610041, China*

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A novel flexible tetradentate ligand 1,6-bis(4′-pyridyl)-2,5-diazahexane (BPDH) was synthesized, and its coordination networks with silver(I) and copper(I) salts chracterized by X-ray single-crystal structure analysis and electrospray mass spectrometry (ES-MS). The network topologies are found to depend greatly on the counter anions and metal ions employed during the reaction and crystallization. The structure of [Ag(BPDH)]NO_3 **1** is a one-dimensional infinite hinged cationic chain in which the counter anions link two adjacent chains through N–H · · · O and C–H · · · O hydrogen bonds. The complex [Ag(BPDH)]ClO_4·CH_3CN **2** is a two-dimensional infinite cationic network; the solvate acetonitrile molecule and counter anions are incorporated in the channels of two adjacent sheets through C–H · · · O, N–H · · · O and N–H · · · N hydrogen bonds. The structure of [Cu(BPDH)]ClO_4 **3** is an infinite two-dimensional cationic grid; the counter anions are located in the voids of two layers through a single C–H · · · O hydrogen bond. The structures of the three co-ordination polymers are stabilized by face-to-face or edge-to-face π–π interactions. The results demonstrate that counter ions and transition metal ions play important roles in the formation of supramolecular frameworks.

Introduction

The construction of inorganic supramolecular arrays based on covalent interactions, hydrogen bonding, or other intermolecular interactions is a rapidly developing area of functional materials.[1–3] Therefore metal complexes with specific network topologies have attracted great interest.[4] The recent efforts in crystal engineering of networked materials based on polymeric co-ordination compounds have been devoted to the use of multifunctional ligands.[5–7] However, the rational design of these materials is complicated by the uncertain co-ordination propensity of the metal ion which is influenced by factors such as the counter ion, solvent and ligand geometry. Generally the network topology can be controlled and modified by selecting the chemical structure of the ligands,[6,8–10] which can lead to special intermolecular interactions, co-ordination geometry of metal ions, inorganic anions,[6] and sometimes the ratio between metal salt and ligand.[7] Thus understanding how these considerations affect metal co-ordination and influence crystal packing is at the heart of controlling co-ordination supramolecular arrays. There is a growing interest in finding alternative approaches for building new inexpensive and easy-to-prepare supramolecular systems. According to these ideas, we designed and synthesized a new flexible tetradentate ligand 1,6-bis(4′-pyridyl)-2,5-diazahexane (BPDH) which may provide a co-ordination model of non-rigidity and versatility.

In order to probe the influence of metal-ion stereochemical preference on the supramolecular construction, a study was carried out with monovalent copper(I) and silver(I) salts having the same perchlorate counter ion and also in order to investigate the influence of the steric requirements and hydrogen-bonding ability of the counter ion on the supramolecular construction we initiated a systematic structural study of silver complexes with different counter ions, *i.e.* perchlorate is tetrahedral and nitrate has a “Y” shape.

Here, we report crystal structures of the BPDH ligand with silver nitrate ($AgNO_3$), silver(I) perchlorate hydrate ($AgClO_4$·H_2O), and copper(I) tetrakis(acetonitrile) perchlorate {[Cu(CH_3CN)$_4$]ClO_4}. The topologies of the ensuing co-ordination networks are found to depend strongly on the counter ions and also have a close relation to the metal ions.

Experimental

General methods

The salt [Cu(CH_3CN)$_4$]ClO_4 was prepared according to the literature method.[11] Solvents such as acetonitrile and methanol were dried and purified by distillation before use. Other reagents were commercially available and used as received without further purification. The C, H and N analyses were made on a Perkin-Elmer 240C elemental analyzer. 500 MHz ^{1}H NMR spectroscopic measurements were performed on a Bruker AM-500 NMR spectrometer, using TMS ($SiMe_4$) as an internal reference at room temperature, electrospray mass spectral measurements on a LCQ System (Finngan MAT, USA) using methanol as mobile phase. The spray voltage, tube lens offset, capillary voltage and capillary temperature were set at 4.50 kV, 0 V, 17.00 V and 150 °C, respectively. The quoted *m*/*z* values are for the major peaks in the isotopic distributions. Thermogravimetric and differential analyses were taken on a simultaneous SDT 2960 thermal analyzer under flowing N_2 with a heating rate of 10 °C min^{-1}.

CAUTION: Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care.

Syntheses

1,6-Bis(4′-pyridyl)-2,5-diazahexane (BPDH). The compound was prepared by modified procedures reported for the synthesis of 1,3-di(2-pyridylmethyleneamino)propane.[12] 7.9 mmol of 1,2-ethanediamine (0.53 ml) were dissolved in 30 ml of absolute

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methanol with refluxing and pyridine-4-carbaldehyde (1.41 ml, 15 mmol) in 30 ml of absolute MeOH was added slowly to give an clear yellowish solution. The mixture was refluxed for 3 hrs and stirred overnight at ambient temperature. Then an excess of sodium tetrahydroborate was added in small portions with stirring at room temperature. The mixture was allowed to stand overnight with stirring and then 30 ml deionized water were added. The solvents were removed by evaporation, and the residue was extracted with chloroform (25 ml × 4). The chloroform solution was evaporated to a syrupy residue under reduced pressure. A colorless powder was obtained by recrystallization of the residue from chloroform and diethyl ether, then washed with diethyl ether and dried in a vacuum. Yield 94%, mp 75–78 °C. ES-MS: *m*/*z* 243.2 (BPDH + H)$^+$: ^{1}H NMR (D_2O, 25 °C): δ 2.58 (s, 4 H); 3.65 (s, 4 H); 7.21 (d, 4 H) and 8.32 (d, 4 H). Found: C, 69.39; H, 7.49; N, 23.00. Calc. for $C_7H_9N_2$: C, 69.39; H, 7.48; N, 23.12%.

[Ag(BPDH)]NO$_3$ 1. All procedures, for example synthesis and recrystallization, were carried out in the dark. A deionized aqueous solution (2 ml) of $AgNO_3$ (17.0 mg, 0.1 mmol) was added dropwise to a stirred solution of BPDH (24.2 mg, 0.1 mmol) in deionized water (3 ml) at room temperature. After filtration, the clear filtrate was allowed to stand at 5 °C for several days, and colourless crystals were collected in 58% yield. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from the filtrate at 5 °C. ^{1}H NMR (CD_3CN, 25 °C): δ 2.88 (s, 4 H); 3.00 (s, 4 H); 7.27 (d, 4 H) and 8.32 (s, 4 H). Found: C, 40.74; H, 4.27; N, 16.74. Calc. for $C_{14}H_{18}AgN_5O_3$: C, 40.80; H, 4.40; N, 16.99%.

[Ag(BPDH)]ClO$_4$·CH$_3$CN 2. All the procedures were carried out in the dark. A solution of $AgClO_4·H_2O$ (22.5 mg, 0.1 mmol) in acetonitrile (10 ml) was added dropwise to a solution of the BPDH (24.2 mg, 0.1 mmol) in methanol (10 ml) with stirring to give a clear solution. Colorless single crystals suitable for X-ray diffraction were obtained in 68% yield by slow diffusion of diethyl ether into the clear filtrate for several days. ^{1}H NMR (CD_3CN, 25 °C): δ 2.85 (s, 4 H); 3.75 (s, 4 H); 7.29 (d, 4 H) and 8.33 (d, 4 H). Found: C, 39.15; H, 4.25; N, 14.25. Calc. for $C_{16}H_{21}AgClN_5O_4$: C, 39.16; H, 4.31; N, 14.27%.

[Cu(BPDH)]ClO$_4$ 3. All the procedures for synthesis and spectral measurements were carried out under an argon atmosphere. Solid BPDH (24.2 mg, 0.1 mmol) was added to a degassed acetonitrile solution (8 ml) of $[Cu(CH_3CN)_4]ClO_4$ (32.7 mg, 0.1 mmol) to give a yellowish solution. Pale yellow single crystals suitable for X-ray diffraction were obtained in 48% yield by slow diffusion of diethyl ether into the clear filtrate for several days. ^{1}H NMR (CD_3CN, 25 °C): δ 2.73 (s, 4 H); 3.78 (s, 4 H); 7.37 (s, 4 H) and 8.58 (s, 4 H). Found: C, 41.45; H, 4.59; N, 13.65. Calc. for $C_{14}H_{18}ClCuN_4O_4$: C, 41.48; H, 4.47; N, 13.82%.

Crystallography

The X-ray diffraction measurements for complexes **1**, **2** and **3** were performed on a Siemens P4 automatic four-circle diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at room temperature. Intensity data were collected in the variable ω-scan mode. The structures were solved by direct methods using SHELXS 86[13] and refined by full-matrix least-squares calculation on F^2 with SHELXL 93.[14] The NO_3^- anion in complex **1** is disordered; each oxygen atom has two positions with the site occupancy factors (s.o.f.s) of 0.5. All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were generated geometrically. Calculations were performed on a PC-586 computer using the Siemens SHELXTL program package.[15,16] Details of the crystal parameters, data collection and refinement for complexes **1**, **2** and **3** are listed in Table 1, and selected bond distances and angles are given in Table 2.

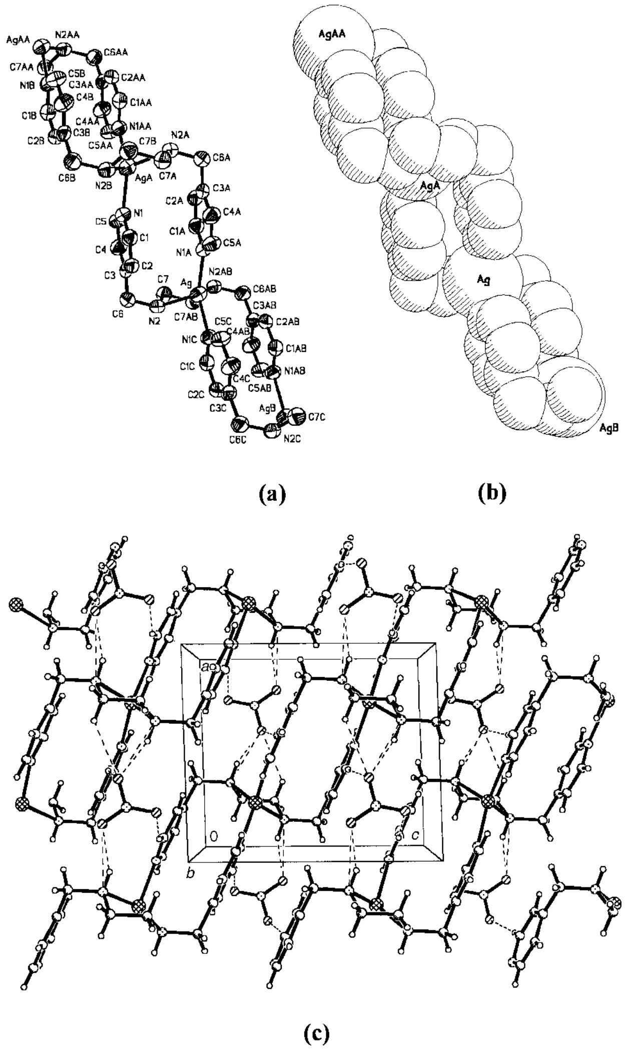


Fig. 1 (a) Cation part of the local co-ordination around the silver(I) atoms in [Ag(BPDH)]NO$_3$ **1** with the ellipsoids drawn at the 50% probability level (as in all figures). (b) Space-filling diagram for **1**. (c) Crystal packing diagram of **1** with hydrogen bonds indicated by dashed lines.

CCDC reference number 186/1783.

See http://www.rsc.org/suppdata/dt/a9/a908910a/ for crystallographic files in .cif format.

Results

Synthesis and crystal structure of complexes 1, 2 and 3

The preparation of the complexes **1**, **2** and **3** is readily accomplished by reactions of silver(I) or copper(I) salt with the ligand 1,6-bis(4′-pyridyl)-2,5-diazahexane (BPDH) in a molar ratio of 1 : 1. The elemental C, H and N analysis and ^{1}H NMR spectra confirmed the chemical formulation for these complexes. The copper(I) complex **3** is quite stable in the solid state, but it is unstable in solution and the acetonitrile or methanol solution of the complex turned to blue within one hour. The silver(I) complexes **1** and **2** are stable to oxygen in both solid and solution states in the dark.

The crystal structure of complex **1** (cation part) is shown in Fig. 1(a) with the atom numbering scheme. Each silver(I) ion is co-ordinated with two N atoms of the ethylenediamine unit of one BPDH, and two N atoms of the pyridyl unit of two other different BPDH ligands. The co-ordination environment of the silver(I) atom is distorted tetrahedral in which the N–Ag–N bond angles vary from 75.93(14) to 122.94(10)° as shown in

Table 1 Summary of crystal data and refinement results for complexes **1**, **2** and **3**

	1	**2**	**3**
Empirical formula	$C_7H_9Ag_{0.5}N_{2.5}O_{1.5}$	$C_{16}H_{21}AgClN_5O_4$	$C_{14}H_{18}ClCuN_4O_4$
Formula weight	206.10	490.70	405.31
T/°C	22(2)	23(2)	23(2)
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2/n$	$P2_1/n$	$P2_12_12_1$
a/Å	8.8060(10)	14.220(2)	9.055(2)
b/Å	9.0430(10)	7.0820(10)	10.734(2)
c/Å	10.2550(10)	19.914(3)	18.338(3)
β/°	91.490(10)	94.330(10)	
U/Å^3	816.36(15)	1999.7(5)	1782.4(6)
Z	4	4	4
μ/mm^{-1}	1.256	1.173	1.400
Measured/independent reflections	2212/1879	4225/3523	2290/2124
R_{int}	0.0119	0.0191	0.0066
$R1$ ($I > 2\sigma(I)$)	0.0354	0.0417	0.0401
$wR2$ ($I > 2\sigma(I)$)	0.0795	0.1094	0.0759

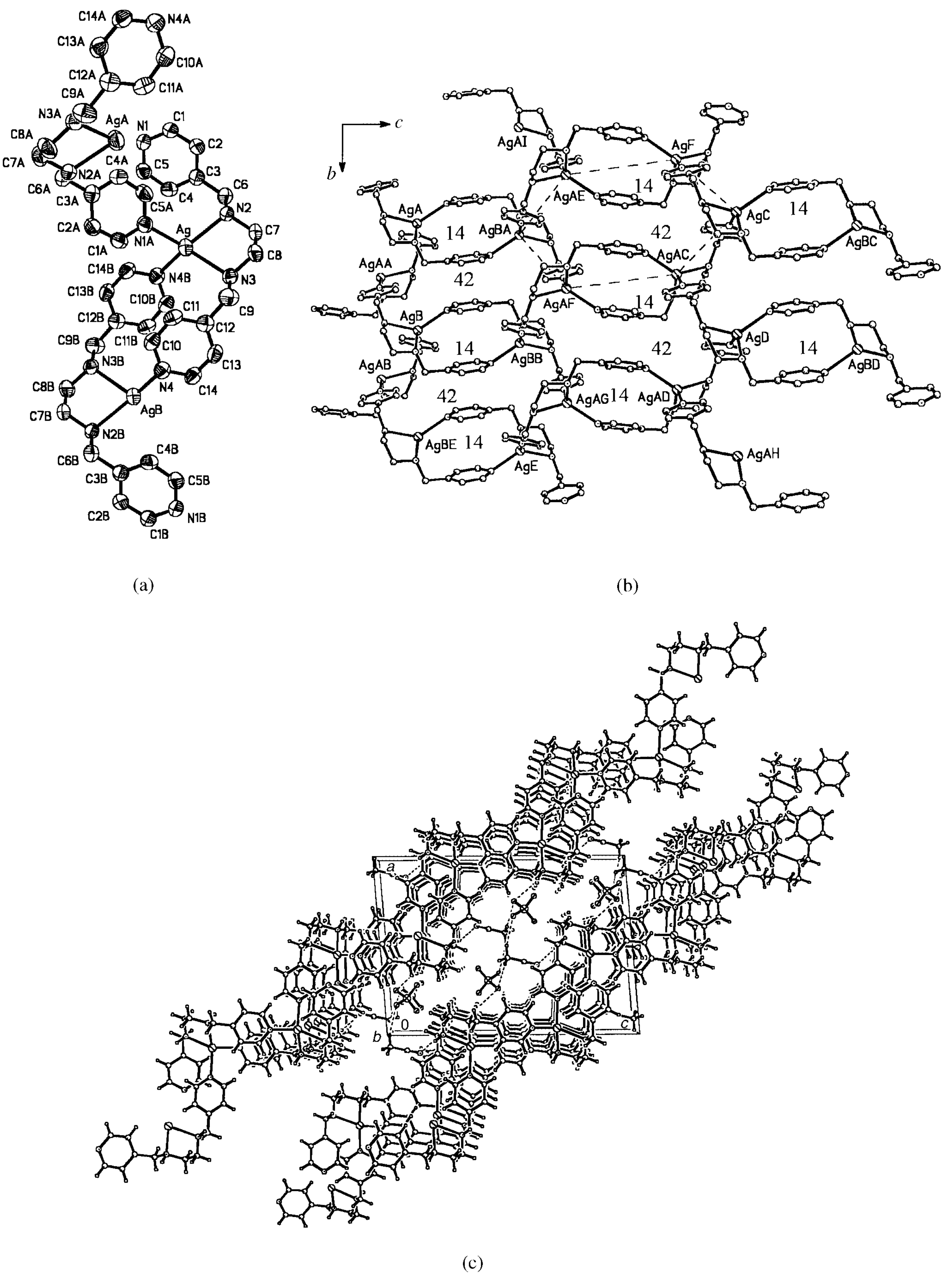
Table 2 Selected bond distances (Å) and angles (°) for complexes **1**, **2** and **3**

[Ag(BPDH)]NO$_3$ **1**			
Ag–N(1)^a	2.301(3)	Ag–N(2)	2.418(3)
(Ag–N)$_{av}$	2.360(3)		
N(1)^a–Ag–N(1)^b	119.65(15)	N(1)^b–Ag–N(2)	104.40(10)
N(2)^c–Ag–N(2)	75.93(14)	N(1)^a–Ag–N(2)	122.94(10)
[Ag(BPDH)]ClO$_4$·CH$_3$CN **2**			
Ag–N(1)^a	2.330(4)	Ag–N(4)^b	2.339(4)
Ag–N(2)	2.351(3)	Ag–N(3)	2.359(4)
(Ag–N)$_{av}$	2.345(4)		
N(1)^a–Ag–N(4)^b	99.06(13)	N(1)^b–Ag–N(2)	113.46(13)
N(4)^b–Ag–N(2)	129.59(13)	N(1)^b–Ag–N(3)	128.89(15)
N(4)^b–Ag–N(3)	111.35(13)	N(2)–Ag–N(3)	77.26(12)
[Cu(BPDH)]ClO$_4$ **3**			
Cu–N(1)^a	2.024(6)	Cu–N(4)^b	2.043(6)
Cu–N(2)	2.132(5)	Cu–N(3)	2.151(5)
(Cu–N)$_{av}$	2.088(6)		
N(1)^a–Cu–N(4)^b	103.9(2)	N(1)^a–Cu–N(2)	114.7(2)
N(4)^b–Cu–N(2)	121.0(2)	N(1)^a–Cu–N(3)	118.3(2)
N(4)^b–Cu–N(3)	114.9(2)	N(2)–Cu–N(3)	84.3(2)

Symmetry transformations used to generate equivalent atoms: ^{a} $-x-1, -y+1, -z+1$; ^{b} $x+\frac{1}{2}, -y+1, z+\frac{1}{2}$; ^{c} $-x-\frac{1}{2}, y, -z+\frac{3}{2}$ for **1**; ^{a} $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; ^{b} $-x+2, -y+3, -z+1$ for **2**; ^{a} $x-\frac{1}{2}, -y+\frac{3}{2}, -z+1$; ^{b} $x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$ for **3**.

Table 2. The average Ag–N bond length of 2.360(3) Å of **1** is quite similar to those of reported silver(I) complexes with the same AgN$_4$ binding site, for example [Ag(ppz)$_2$]$^+$ (ppz = piperazine) exhibits an average Ag–N bond length of 2.386(9) Å.[17] It is noteworthy that in order to achieve a tetrahedral disposition of the four N atoms around each metal ion, three BPDH ligands co-ordinate to one silver(I) ion and each ligand co-ordinates with three metal ions. As shown in Fig. 1(a), each ligand has a "Z" shape to match this kind of co-ordination geometry. Namely the two pyridyl rings (*e.g.* N1, C1, C2, C3, C4, C5 and N1AB, C1AB, C2AB, C3AB, C4AB, C5AB) of each BPDH ligand with a dihedral angle of 6.5° adopt a *trans* conformation with reference to the average plane of ethylenediamine. The dihedral angles AgA–N2A–C6A–C3A and AgA–N2B–C6B–C3B are both −40.6°. Such co-ordination modes produce quadrilaterals (*e.g.* Ag, C6, AgA and C6A in Fig. 1(a)), that join together by sharing Ag atoms, and generate an infinite one-dimensional hinged chain arrangement (Fig. 1(a)). A similar chain-like co-ordination polymer has been reported for a nickel(II) complex of a hexaaza macrocyclic ligand with pendant nitrile groups.[18] The chain-like structure can be seen more clearly from the space-filling diagram shown in Fig. 1(b). Each BPDH ligand serves as a single chain and the second chain joined by the silver atom has a deviation of half a ligand from the first chain. The nitrate counter ions link the two adjacent cationic chains by formation of two N–H···O hydrogen bonds between two oxygen atoms of a NO$_3^-$ and NH groups of two different ligands: r(H···O) = 2.083 and 2.074 Å, and three C–H···O hydrogen bonds between an oxygen atom of NO$_3^-$ and two pyridyl C–H and one ethylene C–H with r(H···O) = 2.407, 2.559 and 2.575 Å as illustrated in Fig. 1(c). These connections generate 2-D-like networks which are stabilized by close face-to-face π–π intrachain and interchain interactions between neighbouring parallel pyridyl rings. The intra- and inter-chain separations between each two pyridyl rings are 3.24 and 3.47 which are close to the separation in graphite (3.35 Å). The Ag···Ag distances are 6.790 (intrachains) and 6.960 Å (interchains).

Fig. 2 shows the crystal structure of complex **2**, in which each Ag is also four-co-ordinated by four nitrogen atoms of three BPDH ligands, as in the structure of **1**. Each BPDH ligand shows a "C" shape with a dihedral angle of 6.4° between the two terminal pyridyl rings. The dihedral angles Ag–N2–C6–C3 and Ag–N3–C9–C12 are 57.3 and 63.4°, respectively, which are different from those of complex **1** as mentioned above. The co-ordination geometry of the metal ion is regarded as distorted tetrahedral with N–Ag–N bond angles varying from 77.26(12)° to 129.59(13)° (Table 2). Six metal ions, *e.g.* AgC, AgF, AgAE, AgBA, AgAF, AgAC, give a hexagon as illustrated in Fig. 2(b). Such a building unit extends along the *b* and *c* axes, and interpenetrates with other units by sharing edges and metal ions. The results of these connections generate a two-dimensional sheet structure with 14- and 42-membered metallacycles (Fig. 2(b)). The similar woven metallacyclic structure of {[Mn-(p-XBP4)$_3$](ClO$_4$)$_2$}$_n$ [p-XBP4 = N,N'-p-phenylenedimethylene-bis(pyridin-4-one)] has been reported.[19] As exhibited in Fig. 2(c), it is obvious that the sheets have a corrugated and wavy network structure.[20] The channels formed between two adjacent sheets are occupied by the perchlorate anions and acetonitrile solvate molecules. The anions and solvate molecules are disposed there by three C–H···O hydrogen bonds generated between three oxygen atoms of different ClO$_4^-$ and the CH$_3$ group of one CH$_3$CN: r(H···O) = 2.443, 2.558, 2.565 Å and one N–H···O hydrogen bond formed between NH of the BPDH ligand and the oxygen atom of ClO$_4^-$ anion with r(H···O) = 2.553 Å. The CN part of the acetonitrile molecule also participates in the formation of one N–H···N hydrogen bond with the NH group of a neighbouring BPDH ligand: r(H···N) = 2.296 Å (Fig. 2(c)). The presence of the solvent CH$_3$CN molecule is also confirmed by thermogravimetric analysis. The TGA spectrum of **2** showed an initial endotherm centred at 115 °C with a weight loss of 8.0% (Calc. 8.3%),



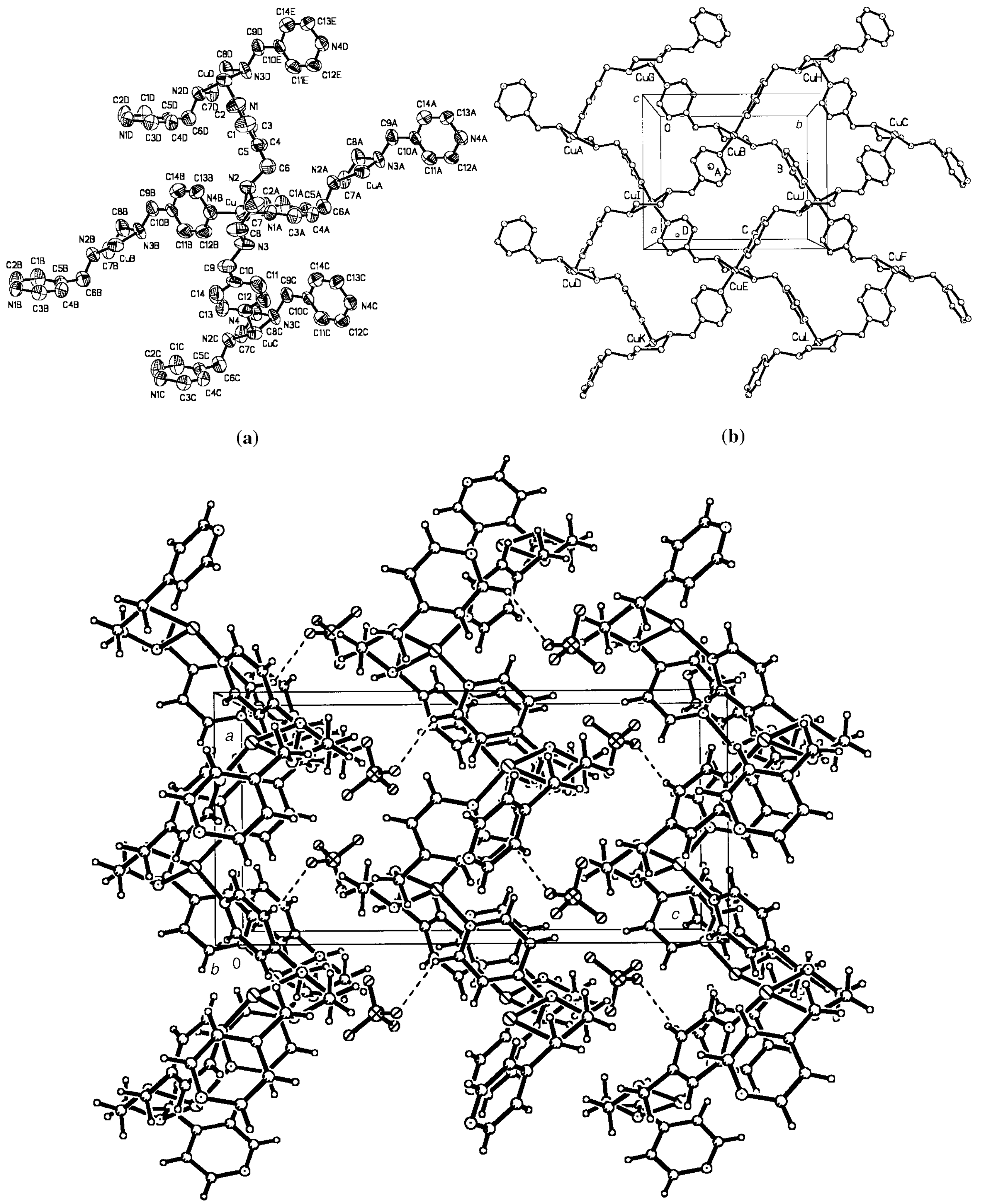
(a)

(b)

(c)

Fig. 2 (a) Part of the cation structure of [Ag(BPDH)]ClO_4·CH_3CN **2** with the atom numbering scheme. (b) Part of the network of **2** with 14- and 42-membered metallacycles. (c) Crystal packing diagram of **2** with hydrogen bonds indicated by dashed lines.

representing the loss of unco-ordinated acetonitrile molecules. The intermetallic Ag···Ag distances are 6.884 and 7.082 Å within quadrilaterals (*e.g.* AgAE and AgF in Fig. 2(b)) and between two adjacent quadrilaterals (*e.g.* AgAC and AgF in Fig. 2(b)), respectively. The distance between AgC and AgF is 7.231 Å. The polymeric structure of complex **2** is also stabilized by close face-to-face π–π interactions since the distances between the two parallel pyridyl rings in each quadrilateral and



(a)

(b)

(c)

Fig. 3 (a) Crystal structure of the cationic moiety of [Cu(BPDH)]ClO$_4$ **3**. (b) Infinite grid structure of **3**. (c) Crystal packing diagram of **3** with hydrogen bonds indicated by dashed lines.

between quadrilaterals are 3.45 and 3.44 Å, respectively (Fig. 2(b)).

In the crystal structure of complex **3** the copper(I) ion is also co-ordinated by four nitrogen atoms from three different BPDH ligands as shown in Fig. 3(a). Each ligand adopts a zigzag form with a dihedral angle of 79.8° between the two terminal pyridyl rings. This dihedral angle is much larger than those of complexes **1** (6.5°) and **2** (6.4°). The dihedral angles Cu–N2–C6–C5 and Cu–N3–C9–C10 are 78.2 and 69.0°, respectively. These are close to the values of **2** but different to those of **1** as described above. The three ligands co-ordinated to one Cu display a crisscross pattern (Fig. 3(a)). Four such building units corrugate by sharing Cu and propagate in the *ab* plane to generate a infinite two-dimensional compressed molecular

Table 3 ES mass spectral data for complexes **1**, **2** and **3**

1		**2**		**3**	
m/*z*	Assignment	*m*/*z*	Assignment	*m*/*z*	Assignment
243.2	$[(BPDH)H]^+$	243.2	$[(BPDH)H]^+$	243.2	$[(BPDH)H]^+$
349.1	$[Ag(BPDH)]^+$	349.2	$[Ag(BPDH)]^+$	305.2	$[Cu(BPDH)]^+$
519.8	$[Ag_2(BPDH)(NO_3)]^+$	389.8	$[Ag(BPDH)(CH_3CN)]^+$	336.8	$[Cu(BPDH)(CH_3OH)]^+$
591.1	$[Ag(BPDH)_2]^+$	591.1	$[Ag(BPDH)_2]^+$	345.9	$[Cu(BPDH)(CH_3CN)]^+$
761.9	$[Ag_2(BPDH)_2(NO_3)]^+$	798.9	$[Ag_2(BPDH)_2(ClO_4)]^+$	547.1	$[Cu(BPDH)_2]^+$
930.7	$[Ag_3(BPDH)_2(NO_3)_2]^+$	1006.7	$[Ag_3(BPDH)_2(ClO_4)_2]^+$	711.0	$[Cu_2(BPDH)_2(ClO_4)_2]^+$
1174.7	$[Ag_3(BPDH)_3(NO_3)_2]^+$			872.7	$[Cu_3(BPDH)_2(ClO_4)_2]^+$
1345.5	$[Ag_4(BPDH)_3(NO_3)_3]^+$			1119.0	$[Cu_3(BPDH)_3(ClO_4)_2]^+$
				1278.6	$[Cu_4(BPDH)_3(ClO_4)_3]^+$

grid (Fig. 3(b)). Similar polymeric structures have been reported for $[Cd(L)_{1.5}](NO_3)_2$ [L = 1,4-bis(4-pyridylmethyl)-benzene] and $[Ag_2(bpethy)_5][BF_4]_2$ [bpethy = 1,2-bis(4-pyridyl)ethyne].[4a,21] The co-ordination geometry of the copper atoms in **3** is also distorted tetrahedral with the N–Cu–N bond angles ranging from 84.3(2) to 121.0(2)°.[22] The pleated cationic layers are shown in Fig. 3(c) and channels occupied by the ClO_4^- anions are created between the two adjacent cationic layers. There is one C–H···O [r(H···O) = 2.425 Å] hydrogen bond between the ClO_4^- and pyridyl ring of the adjacent ligand. The whole structure is stabilized by T-type edge-to-face π–π interactions.[23] As shown in Fig. 3(b), the centroid–centroid distances between each two pyridine rings A and B, A and C, A and D, B and C, C and D are 5.79, 5.48, 5.37, 5.49 and 5.48 Å, respectively and the dihedral angles between these two pyridine rings are 53.3, 79.8, 54.0, 55.1 and 53.3°. The Cu···Cu separations are 7.481 (CuI···CuB, CuI···CuE) and 7.533 Å (CuB···CuJ, CuE···CuJ) as indicated in Fig. 3(b).

Electrospray (ES) mass spectra

The complexes **1**, **2** and **3** were also investigated by ES mass spectrometry and the spectral data are summarized in Table 3. The ES mass spectrum of complex **1** in methanol solution is shown in Fig. 4(a). Eight peaks were observed which correspond to mono-, di-, tri- and tetra-nuclear species. All the assignments are ensured by good agreement between the observed and calculated isotopic distributions. Fig. 4(b) shows a typical example of a comparison between the experimental and calculated isotope distributions for the peak at m/z = 761.9. The ES mass spectrum of **2** in methanol solution displayed six peaks, which are from mono- to tri-nuclear species. The appearance of $[Ag(BPDH)(CH_3CN)]^+$ at m/z = 389.8 further confirms the presence of a crystal acetonitrile molecule which is stabilized by C–H···O and N–H···N hydrogen bonds as mentioned above. Nine peaks were obtained from the ES mass spectrum of the **3** in acetonitrile solution. The peak of $[Cu(BPDH)(CH_3OH)]^+$ at m/z 336.8 contains a methanol molecule since the methanol was used as mobile phase. The cationic species observed in the above ES mass spectra derived from the architectures of **1**, **2** and **3** suggest polymeric structures in solution.

Discussion

From the present study it was found that the tetradentate BPDH ligand is versatile and affords different types of framework complexes with different counter ions and transition metal ions. The flexibility of the BPDH ligand stemming from its length and composition is unique. A di-Schiff base ligand obtained from pyridine-2-carbaldehyde and ethane-1,2-diamine and its silver(I) complexes have been reported.[24] It forms dinuclear double-stranded helical complexes with silver(I) tetrafluoroborate.[24] When (1*R*,2*R*)-cyclohexane-1,2-diamine was used instead of ethane-1,2-diamine, its di-Schiff base ligand with pyridine-2-carbaldehyde reacted with silver(I) nitrate to give a homochiral single-stranded C_2-co-ordination polymer. In our BPDH ligand the terminal units are 4-substituted pyridine and there are no C=N double bonds, *i.e.* it is a reduced Schiff base. Therefore BPDH did not provide a dinuclear helical complex even when treated with silver(I) tetrafluoroborate.[25] Instead, an infinite two-dimensional network was obtained by reaction with $AgClO_4$ or $AgBF_4$. The different structures obtained from these reactions can be described as the results of reading molecular information stored in the ligand by the metal ion.

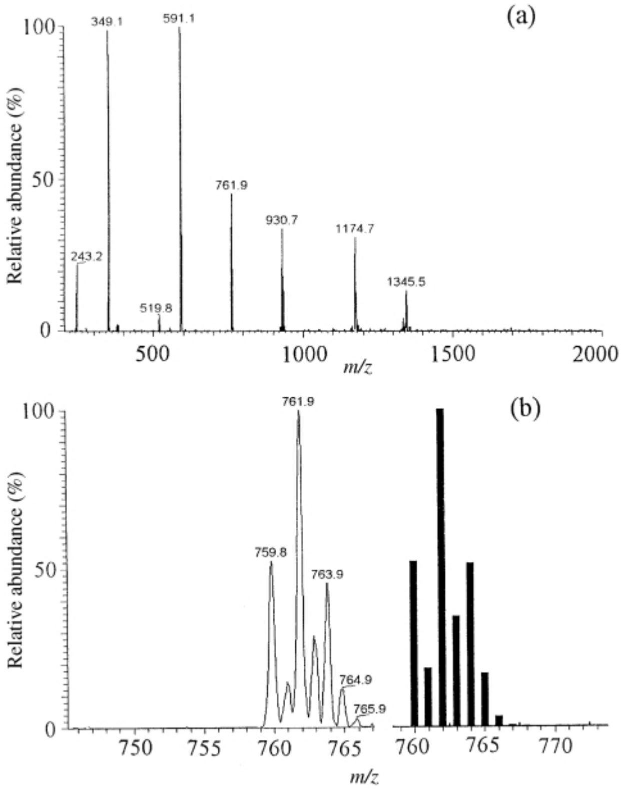


Fig. 4 (a) The ES mass spectrum of $[Ag(BPDH)]NO_3$ **1** in methanol solution. (b) The observed (traces) and calculated (bars) isotopic distributions for the peak at m/z 761.9.

On the other hand, it is noteworthy that the different structures of complexes **1** and **2** demonstrate that the counter ions play important roles in the construction of supramolecular networks. It has been reported that diverse conformations can be achieved by subtle changes in the counter ions.[20,26] In our cases, NO_3^- has a "Y" shape while the ClO_4^- is a tetrahedral. Thus the ClO_4^- is not expected to form directional hydrogen bonds as the NO_3^- does as shown in Figs. 1(c) and 2(c). All three oxygen atoms of each NO_3^- in complex **1** participate in the formation of N–H···O or C–H···O hydrogen bonds (Fig. 1(c)). In the case of **2** there is only one N–H···O hydrogen bond between the ClO_4^- and BPDH ligand in addition to three other C–H···O hydrogen bonds between the ClO_4^- and solvent acetonitrile molecule (Fig. 2(c)).

The structures of complexes **2** and **3** imply that the reaction is also influenced by the nature of the metal ions employed in addition to the counter ions. The co-ordination environments of silver(I) and copper(I) atoms in these complexes are both distorted tetrahedral with a N_4 donor set. Hence, the different structures of **2** and **3** are considered to be caused by the different atomic radii of Ag^I (1.13 Å) and Cu^I (0.96 Å). Thus, we can obtain rationally designed arrays by subtle selection of metal ions and counter ions. Further studies of the reaction of the BPDH ligand with other transition metal ions are in progress in our laboratory.

Finally, ES mass spectrometry (ES-MS) has been proved to be a soft ionization method and allows the characterization of supramolecular complexes. It has been used to obtain information on intermediate kinetic species and the formation pathway of supramolecular complexes.[27] However, up to now not much has been reported for co-ordination polymers. In the present work ES-MS was employed to study the supramolecular networks. The observation of mono- to tetra-nuclear species suggested the existence of polymeric structures of complexes **1**, **2** and **3** under the ES-MS conditions (Table 3). Furthermore, it should be noted that no multiply charged species were observed under our experimental conditions.

Conclusions

Three novel co-ordination polymers of the BPDH ligand with silver(I) and copper(I) salts have been prepared and characterized by single crystal X-ray diffraction. An infinite one-dimensional hinged cationic chain is formed with $AgNO_3$ and the NO_3^- ions link two adjacent chains through hydrogen bonds. A two-dimensional cationic sheet was obtained when the perchlorate salt was used instead of nitrate. The ClO_4^- and CH_3CN molecule are incorporated between the channels formed between two adjacent sheets through intermolecular hydrogen bonds. In the case of copper(I), the reaction of the BPDH ligand with $[Cu(CH_3CN)]ClO_4$ gives an infinite compressed two-dimensional cationic grid and the ClO_4^- are disposed between two layers through hydrogen bonds. The polymeric networks are stabilized by face-to-face π–π interactions for **1** and **2**, and T-shape edge-to-face π–π interactions for **3**. Therefore, the results of this study not only illustrate that the metal ions play important roles in the construction of supramolecules, but also give a nice example of anion controlled polymeric architecture construction. The present study also demonstrates that the hydrogen bonds together with π–π interactions co-affect inorganic supramolecular formation.

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