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Metal ion-assisted assembly of one-dimensional polyrotaxanes incorporating cucurbit[6]uril

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Three cucurbit[6]uril (CB[6])-based polyrotaxanes [Cu(H_2**C6N4**)(CB[6])]Cl_4·12H_2O (**1**), [Co(H_2**C6N4**)(CB[6])]Cl_4·14H_2O (**2**) and [Ag(**C6N4**)(CB[6])]NO_3·7H_2O (**3**) are prepared using *N*,*N*′-bis(4-pyridylmethyl)-1,6-hexanediamine (**C6N4**) threading into CB[6]'s and metal ions' assistance. Single-crystal X-ray diffraction analyses reveal that polyrotaxanes **1**, **2** and **3** all have 1D chain structure where **1** and **2** are linear and **3** has two shapes, linear and sawtooth, respectively. The effects of guest molecules, metal and counter ions as well as intermolecular weak interactions on the architectures of polyrotaxanes are discussed.

Keywords: metal ion; cucurbit[6]uril; polyrotaxane; crystal engineering

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Introduction

As one type of supramolecular assembly consisting of ring, string and stoppers, rotaxane and polyrotaxane have received considerable attention for a long time because of their specific topology, structures and interesting properties as well as their potential applications in the field of molecular devices and machines, nanometre material, crystal engineering and so on (*1–5*). Cucurbit[6]uril (CB[6]) is a hexameric macrocyclic compound having a rigid and pumpkin-shaped macrocavity with two highly polar carbonyl openings. As one of an important ring part of rotaxanes, CB[6] can easily form inclusion complexes with aliphatic diammonium ions. This makes (CB[6]) attractive as a building block for the construction of 1D, 2D and 3D polyrotaxanes and molecular necklaces (*6–9*). Nevertheless, the shape and structure of polyrotaxane are not yet controllable, and the factors effecting on them need to be found. Recently, we have reported the preparation and crystal structures of a kind of silver(I) ion-assisted CB[6]-based 1D polyrotaxanes incorporating pyridyl-stopped aliphatic or aromatic diamine guests, i.e. *N*,*N*′-bis(3-pyridylmethyl)-1,6-hexanediamine (**C6N3**) or *N*,*N*′-bis(3-pyridylmethyl)-1,4-benzenedimethylamine (**BDMN3**); the structure parameters to distinguish their shapes were also proposed (*10*). For further studying the effects of guest molecules on the shape and structure of polyrotaxanes, we designed and synthesised a new aliphatic diaminoalkane guest, *N*,*N*′-bis(4-pyridylmethyl)-1,6-hexanediamine (**C6N4**) (Scheme 1), and prepared polyrotaxanes of it with CB[6] and various metal salts. Herein, we report the crystal structures and thermal properties of three metal ion-assisted CB[6]-based polyrotaxanes, namely [Cu(H_2**C6N4**)(CB[6])]Cl_4·12H_2O (**1**), [Co(H_2**C6N4**)(CB[6])]Cl_4·14H_2O (**2**) and [Ag(**C6N4**)(CB[6])]NO_3·7H_2O (**3**), respectively. The influence of guest molecules, metal and counter ions, and intermolecular weak interactions on the architectures of polyrotaxanes are discussed.

Results and discussion

Crystal structure of polyrotaxane [Cu(H_2C6N4)(CB[6])]Cl_4·12H_2O (1)

The X-ray crystallographic analysis demonstrated that **1** is an infinite 1D polyrotaxane connected by Cu(II), in which the methylene chain of [H_2**C6N4**]$^{2+}$ threads into the cavity of CB[6] (Figure 1(a)). Each Cu(II) ion is coordinated by two nitrogen atoms from two pyridyl groups of two opposite [H_2C6N4]$^{2+}$ and four chloride ions. According to the bond lengths and angles (Table 1), the coordination geometry of Cu(II) can be described as a distorted octahedron. The two coordinated pyridine planes have a *trans* conformation since the two 4-pyridyl nitrogen atoms are located in a direction opposite to that of the Cu(II) ion. The Cu1—N13 bond length of 2.012(15) Å (Table 1) is similar to those reported for copper(II) complexes with homologous protonated diaminoalkane ligands (*9, 11*).

It can be seen from Figure 1(b) that there are two C—H···Cl hydrogen bonds with C···Cl distances of 3.338(13) and 3.40(3) Å (Table S1), formed by two

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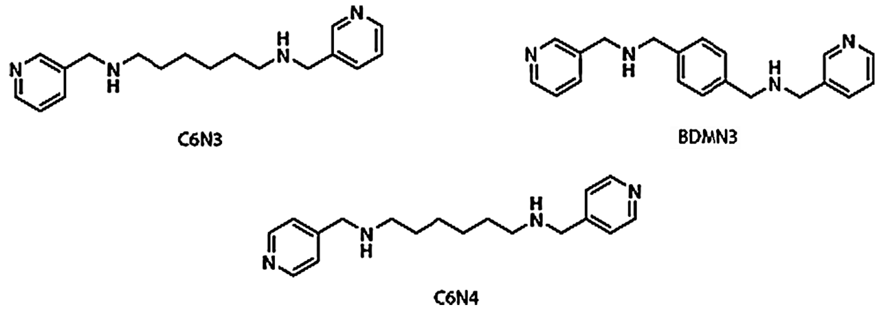

Scheme 1. Schematic drawing of aliphatic diaminoalkane guests.

methine C atoms of CB[6] in the polyrotaxane and the coordinated chlorine ion from the adjacent 1D polyrotaxane, respectively, and one C—H···O hydrogen bond with a C···O distance of 3.296(62) Å (Table S1), formed by the carbonyl O atom of CB[6] in the polyrotaxane and the methylene C atom of $[H_2\mathbf{C6N4}]^{2+}$ from the adjacent 1D polyrotaxane. Moreover, a π–π interaction was observed in **1**, since the plane of the pyridyl group in one chain almost parallels with the semi-glycoluril ring of CB[6] from the nearby chain with a centre-to-centre distance of 3.66 Å. These intermolecular weak interactions generate an infinite 2D network structure of **1** (Figure 1(b)). Furthermore, the 2D networks pack together to give a 3D structure of **1** (Figure S1), which is stabilised by weak interactions between the lattice water molecule and the polyrotaxane.

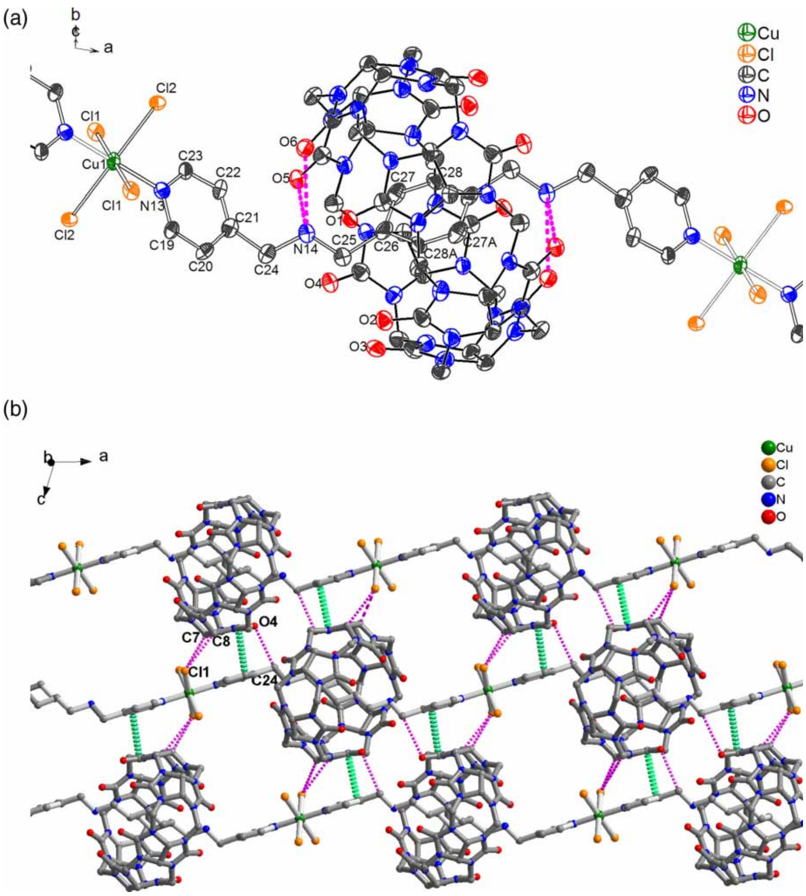

Figure 1. (a) X-ray crystal structure of polyrotaxane **1**. The thermal ellipsoids are drawn at 30% probability. (b) 2D structure of **1**. Weak interactions are indicated by dashed lines: violet, hydrogen bonds; green, π–π interactions. The hydrogen atoms and water molecules are omitted for clarity.

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

$[Cu(H_2\mathbf{C6N4})(CB[6])]Cl_4\cdot 12H_2O$ **1**[a]			
Cu1—N13	2.012(3)	Cu1—Cl1	2.2894(8)
Cu1—Cl2	2.4107(9)	N13—Cu1—N13#1	180.00(18)
N13—Cu1—Cl1	90.16(8)	N13#1—Cu1—Cl1	89.84(8)
N13—Cu1—Cl1#1	89.84(8)	N13#1—Cu1—Cl1#1	90.16(8)
Cl1—Cu1—Cl1#1	180.00(2)	N13—Cu1—Cl2	90.50(7)
N13#1—Cu1—Cl2	89.50(7)	Cl1—Cu1—Cl2	91.72(4)
Cl1#1—Cu1—Cl2	88.28(4)	N13—Cu1—Cl2#1	89.50(7)
N13#1—Cu1—Cl2#1	90.50(7)	Cl1—Cu1—Cl2#1	88.28(4)
Cl1#1—Cu1—Cl2#1	91.72(4)	Cl2—Cu1—Cl2#1	180.00(3)
$[Co(H_2\mathbf{C6N4})(CB[6])]Cl_4\cdot 14H_2O$ **2**[a]			
Co1—N13	2.144(2)	Co1—Cl1	2.1784(8)
Co1—Cl2	2.3153(8)	N13—Co1—N13#1	180.000(1)
N13#1—Co1—Cl1#1	90.41(6)	N13—Co1—Cl1#1	89.59(6)
N13#1—Co1—Cl1	89.59(6)	N13—Co1—Cl1	90.41(6)
Cl1#1—Co1—Cl1	180.00(3)	N13#1—Co1—Cl2#1	90.04(7)
N13—Co1—Cl2#1	89.96(7)	Cl1#1—Co1—Cl2#1	91.76(3)
Cl1—Co1—Cl2#1	88.24(3)	N13#1—Co1—Cl2	89.96(7)
N13—Co1—Cl2	90.04(7)	Cl1#1—Co1—Cl2	88.24(3)
Cl1—Co1—Cl2	91.76(3)	Cl2#1—Co1—Cl2	180.000(1)
$[Ag(\mathbf{C6N4})(CB[6])]NO_3\cdot 7H_2O$ **3**			
Ag1—N25	2.038(2)	Ag2—N27	2.164(2)
N25—Ag1—N25	180.00(11)	N27—Ag1—N27	180.00(14)

[a] Symmetry transformations used to generate equivalent atoms; #1: $-x + 1.5, -y + 1.5, -z$.

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Crystal structure of polyrotaxane $[Co(H_2C6N4)(CB[6])]Cl_4\cdot 14H_2O$ (2)

When Co^{2+} was used to replace the Cu^{2+} in **1**, the polyrotaxane **2** was obtained successfully in which Co^{2+} is coordinated by the pyridyl N of the pseudo-rotaxane $[(H_2\mathbf{C6N4})(CB[6])]Cl_2$. As illustrated in Figure 2, **2** is an isomorphous 1D polyrotaxane with a shape similar to that of **1** but with different amounts of solvent water. Based on the bond lengths and angles of **2** (Table 1), the coordination geometry of Co(II) can also be described as a distorted octahedron like Cu(II) in **1**, and the two coordinated pyridine planes have a *trans* conformation too. The Co1–N13 bond length of 2.144(15) Å (Table 1) is similar to those reported for cobalt(II) complexes with the homologous protonated diaminoalkane ligands (*9*).

The 2D network structure of **2** is also very similar to that of **1**, which is stabilised by two C—H···Cl hydrogen bonds with C···Cl distances of 3.369(12) and 3.435(29) Å (Table S1), one C—H···O hydrogen bond with a C···O distance of 3.300(62) Å (Table S1), and a π–π interaction between the plane of the pyridyl group and the semi-glycoluril ring of CB[6] with a centre-to-centre distance of 3.65 Å (Figure 2(b)). Similarly, the 2D networks pack together to give a 3D structure of **2** (Figure S2), which is stabilised by weak interactions between the lattice water molecule and the polyrotaxane.

Crystal structure of polyrotaxane $[Ag(C6N4)(CB[6])]NO_3\cdot 7H_2O$ (3)

When $AgNO_3$ was added to the $[(H_2\mathbf{C6N4})(CB[6])](NO_3)_2$ solution, polyrotaxane **3** was obtained. From X-ray crystallographic analysis it is worth noting that **3** contains two types of polyrotaxanes, i.e. forms **A** and **B**, respectively (Figure 3). In the pseudo-rotaxane unit of form **A**, the dihedral angle between the plane of six portal carbonyl O atoms of CB[6] and the plane of pyridyl group of $(H_2\mathbf{C6N4})^{2+}$ is 85.39°, and in **B** the corresponding angle is 31.57°. The protonated amine nitrogen atoms of $(H_2\mathbf{C6N4})^{2+}$ protrude 0.84 and 0.79 Å outside the plane of the six portal carbonyl O atoms, in **A** and **B**, respectively. Each Ag(I) ion with a linear coordination geometry in **3** sits on an inversion centre and is coordinated by two nitrogen atoms from two parallel pyridyl groups of two $[H_2\mathbf{C6N4}]^{2+}$ ligands with a *trans* conformation. The Ag–N bond lengths of 2.038(3) Å (**A**) and 2.163(3) Å (**B**) (Table 1) are shorter than those in the previously reported silver(I) complexes with the homologous protonated diaminoalkane ligands (*6, 7, 9, 10, 12*). Moreover, silver(I) ion in **B** has a weak interaction with the nitrate anion [the Ag2···O13 distance is 2.669(7) Å (Table S2)] similar to that observed in the previously reported silver(I) complexes (*4*). Whereas more interestingly, the Ag1···O10 distance of 2.849(3) Å (Table S2) indicates that there is a weak interaction between the Ag1(I) ion in **A** and the carbonyl O atom of CB[6] in **B**

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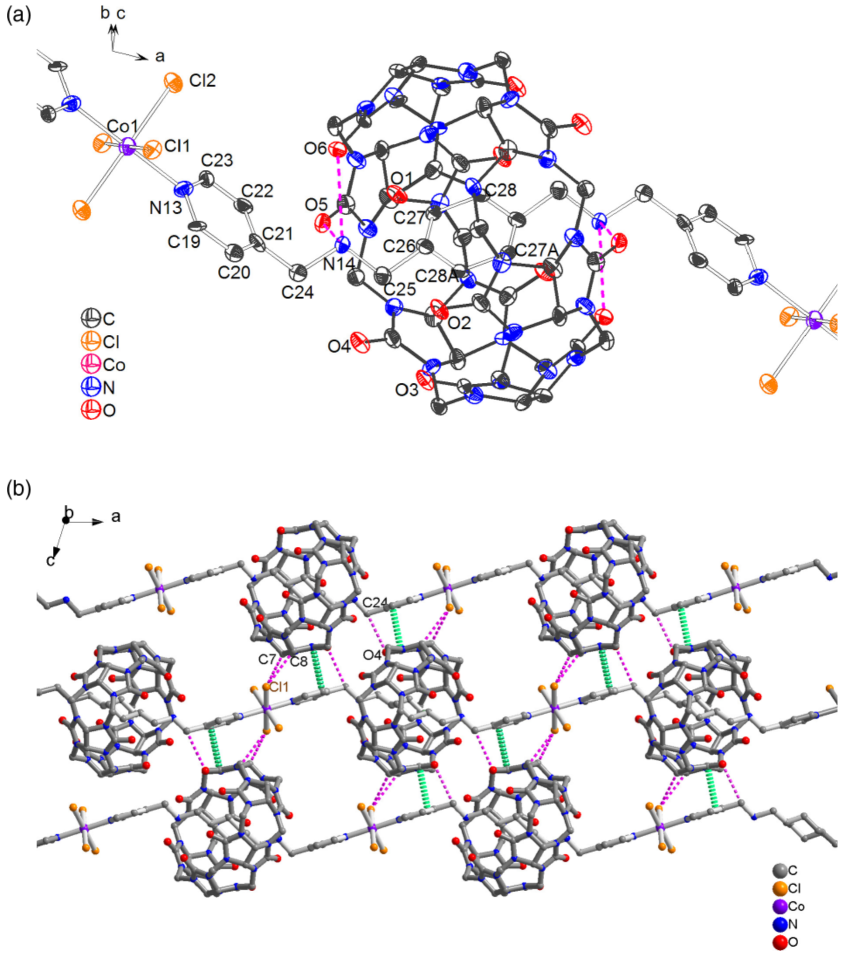

Figure 2. (a) X-ray crystal structure of polyrotaxane **2**. The thermal ellipsoids are drawn at 30% probability. (b) 2D structure of **2**. Weak interactions are indicated by dashed lines: violet, hydrogen bonds; green, π–π interactions. The hydrogen atoms and water molecules are omitted for clarity.

(Figure 3(a)). In addition, there are two C—H···O hydrogen bonds with the C···O distances of 3.207(5) and 3.227(5) Å (Table S1) formed by the carbonyl O atoms of CB[6] in the polyrotaxane **A** and the methylene C atoms of CB[6] from the adjacent polyrotaxane **B**, respectively. Furthermore, the plane of the pyridyl in **B** almost parallels with the semi-glycoluril ring of CB[6] in **A** with a centre-to-centre distance of 3.74 Å, which implies that there is a π–π interaction between the above two planes (Figure 3(b)). These three kinds of weak interactions stabilise the 3D structure of **3** formed by interlaced packing of the 2D planes composed of **A** or **B**, respectively (Figure 4). The weak interactions among lattice water molecule, nitrate anion and the 1D chain also help to stabilise the 3D structure of **3**.

The shapes of 1D polyrotaxanes

In our previous report (*10*), the effects of ligand (guest molecules) and counterions on the structures of polyrotaxanes were discussed, and three structure parameters, θ_1, θ_2 and ω (Scheme 2) have been defined to distinguish the various shapes of the 1D polyrotaxanes. If $\omega = 0°$, a linear ($\theta_1 = \theta_2 < 45°$) or a sawtooth-wave ($\theta_1 = \theta_2$, and $45° < \theta < 90°$) shaped 1D polyrotaxane was obtained. If $45 < \omega < 90°$, the shape of 1D polyrotaxane will be square-wave ($\theta_1 = \theta_2$) or helix ($\theta_1 \neq \theta_2$ and the pyridine group bending in the same direction).

According to the above criteria and experimental structural parameters (Table 2), **1**, **2** and **3A** have similar linear shapes and structures, and only **3B** has a sawtooth-wave shape.

The above structural and shape fact could be explained by the coordination geometry of metal ions. Cu(II) and Co(II) usually assume the same six-coordinated geometry. When the four chloride anions are located in the plane of the coordination octahedron, two pyridyl groups of the guests will coordinate with the metal ions in a linear mode. Therefore, the coordination geometry is one of the key effects for the shape of polyrotaxane.

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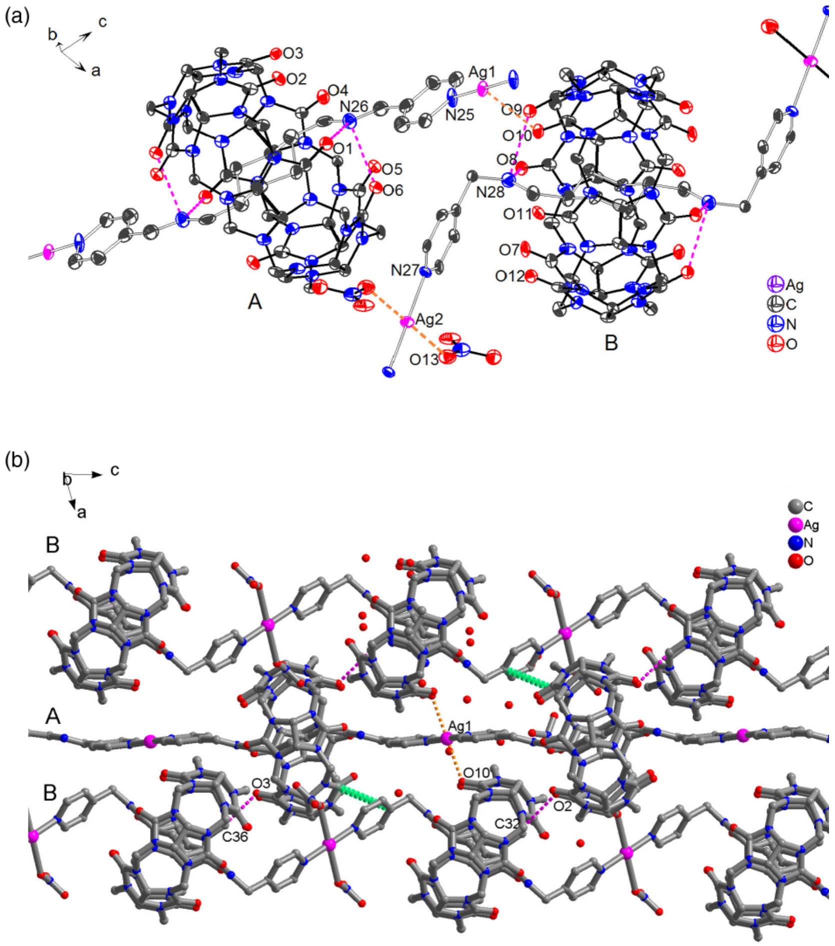


Figure 3. (a) X-ray crystal structure of polyrotaxane **3**. The thermal ellipsoids are drawn at 30% probability. (b) 3D structure of **3**. Weak interactions are indicated by dashed lines: orange, Ag···O interactions; violet, hydrogen bonds and green, π–π interactions. The hydrogen atoms of some water molecules are omitted for clarity.

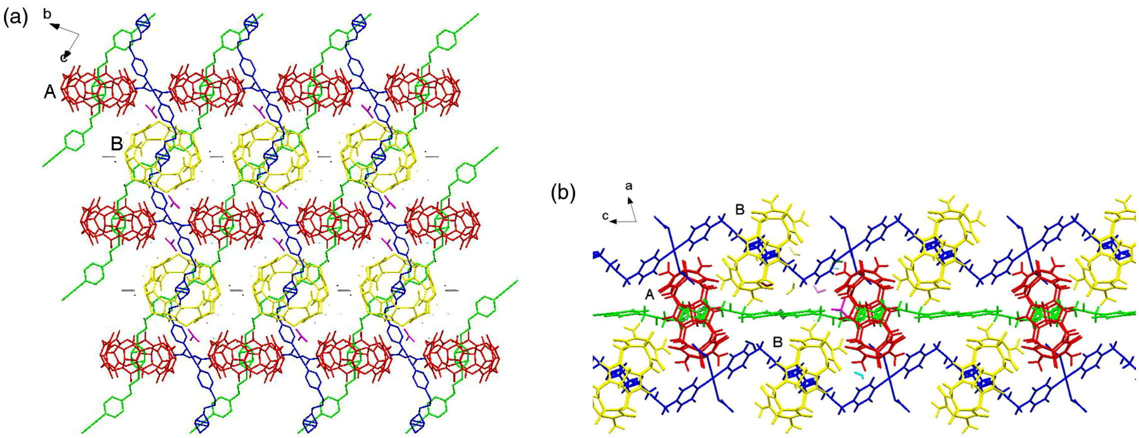
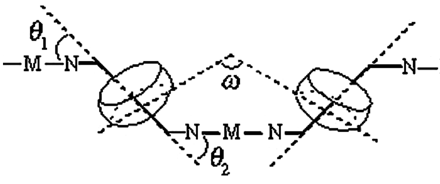


Figure 4. 3D structure of **3** formed by interlaced packing of the 2D planes composed of **A** or **B**, viewed along (a) *a*-axis or (b) *b*-axis.



Scheme 2. Structure parameters for polyrotaxane. θ_1, θ_2: dihedral angle between the plane formed by atoms of aliphatic or aromatic spacer and the plane of pyridine group in protonated diaminoalkane guest. ω; Dihedral angle between the planes of the six portal carbonyl O atoms of two adjacent CB[6].

Moreover, the Ag(I) ion can also have a linear coordination geometry. Therefore, **1**, **2** and **3A** all have linear 1D structure, but the flexibility of the guest makes their pyridyl groups bend more, leading the θ_1, θ_2 of **3B** close to 90° which might result in the sawtooth-shaped structure of **3B**. However, the polyrotaxanes formed by $Cu(NO_3)_2$ and $Co(NO_3)_2$ with CB6 and aliphatic diaminoalkane guests reported by Kim's group take on various shapes other than the linear one (*9*). Therefore, probably, the anion ligands also affect the shape of the polyrotaxane formed by linking pseudo-rotaxane with metal ions. It worth noting that, when compared with the polyrotaxane formed by *N*,*N*′-bis(3-pyridylmethyl)-1,6-hexanediamine(**C6N3**), CB[6] and $AgNO_3$ (*10*), **C6N4** in the above-mentioned polyrotaxanes has a 4-pyridyl terminal group, which easily makes the polyrotaxane bend less than the 3-pyridyl terminal group after coordination with metal ions. Thus, the polyrotaxanes **1**, **2** and **3** have less bending and more rigid 1D linear or sawtooth-wave-like structure, while the polyrotaxane [Ag(H_2**C6N3**)(CB[6])]$(NO_3)_3 \cdot 8H_2O$ adopts the square-wave shape (*10*). In addition, *N*,*N*′-bis(2-pyridylmethyl)-1,6-hexanediamine (**C6N2**) is difficult to form the polyrotaxane with CB[6] and metal ion, since the *ortho*-substituted pyridine groups lead to the pyridyl nitrogen atoms being so close to the polar carbonyl openings of CB[6] that metal ions could not coordinate with the pyridine groups easily due to the steric hindrance. In this case, we obtained a supramolecular adduct of the pseudo-rotaxane formed by **C6N2** and CB[6], and the six-hydrated Zn(II) ion (*13*). Therefore, the relative position of the substituent at the terminal pyridyl groups of aliphatic diaminoalkane guests has an important effect on the formation of 1D polyrotaxane and its shape.

Table 2. Structure parameters (°) for polyrotaxane **1**, **2** and **3**.

Polyrotaxane	θ_1, θ_2	ω	Shape
1	39.82, 39.82	0	Linear
2	39.19, 39.19	0	Linear
3	**A** 20.34, 20.34	0	Linear
	B 87.30, 87.30	0	Sawtooth-wave

TGA study

It is expected that the stability of the guest will be improved after it threads into the cavity of CB[6] and is coordinated by metal ions. Therefore, the thermal gravity analysis (TGA) experiment was carried out in nitrogen to examine the thermal stability of the polyrotaxanes. The result suggests that for the polyrotaxane **1**, the first weight loss (22%) between room temperature and 300 °C corresponds to the loss of the water molecules and chlorine ions of the compound. The second weight loss between 300 and 600 °C (50%) corresponds to the decomposition of H_2**C6N4**$^{2+}$ and CB[6]. The two peaks at 418.9 and 465.8 °C in the derivative weight curve of **1** are about 100–150 °C higher than that of **C6N4** (314.2 °C), proving that polyrotaxane **1** has a good thermal stability (Figure S3). Polyrotaxane **2** and **3** also have a better thermal stability than the guest (Figure S3).

Conclusion

In this paper, we report the crystal structures of three metallo-polyrotaxanes consisting of **C6N4** and CB[6]. Linked by different metal ions, pseudo-rotaxane units of [(H_2**C6N4**)(CB[6])]$^{2+}$ generate three, 1D chain polyrotaxanes, **1**, **2** and **3**, respectively. The shapes of the 1D polyrotaxane chains are affected by the coordination geometry of metal ions, the flexibility and substituent relative position of methylene C for terminal pyridyl N in the guests, as well as the counter anion ligands. Intermolecular weak interactions play an obvious role in generating infinite two- and 3D structures from 1D chains of the polyrotaxanes. The results of TGA suggest that the stability of **C6N4** can be improved after being included in the cavity of CB[6] and coordinated by metal ions in polyrotaxanes.

Experimental section

General methods

All commercially available chemicals are of reagent grade and used as received without further purification. Elemental analysis was carried out on a Perkin-Elmer 240 °C elemental analyser. ^{1}H NMR spectra were recorded on a Brucker DRX500 NMR spectrometer. TGA was carried on a Perkin-Elmer thermal analyser. **C6N4** was synthesised according to literature procedures (*9*) just replacing 1,4-butadiamine with 1,6-hexanediamine. CB[6] were prepared by procedures reported previously (*8*). All procedures for synthesis and measurements of the silver(I) complex were carried out in dark.

Preparation of [(H_2**C6N4**)(CB[6])]Cl_2 CB[6] (1.39 g, 1.20 mmol) and **C6N4** (0.30 g, 1.00 mmol) were mixed in HCl solution (pH 5, 20 ml). After the mixture was stirred at room temperature for 3 h, the undissolved CB[6] was filtered off. The filtrate was

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Table 3. Crystallographic data for crystals **1**–**3**.

Crystal	**1**	**2**	**3**
Chemical formula	$CuC_{54}H_{64}Cl_4N_{28}O_{12}\cdot 12H_2O$	$Co_2C_{108}H_{128}Cl_8N_{56}O_{24}\cdot 28H_2O$	$AgC_{54}H_{62}N_{29}O_{15}\cdot 7H_2O$
Formula weight	1718.86	3500.57	1591.31
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	C2/c	C2/c	P − 1
a (Å)	21.384(7)	21.573(4)	14.6980(10)
b (Å)	25.493(6)	25.483(5)	15.0847(10)
c (Å)	18.919(4)	18.960(4)	19.0236(13)
α (°)	90.00	90.00	76.7150(10)
β (°)	107.54(3)	107.65(3)	70.4340(10)
γ (°)	90.00	90.00	72.9950(10)
V (Å)^3	9834(4)	9933(4)	3759.6(4)
Z	4	2	2
λ (Å)	0.71073	0.71073	0.71073
$D_{\text{calcd.}}$ (g cm^{-3})	1.161	1.170	1.406
T (K)	293	293	298(2)
μ (Mo K$_\alpha$) (mm^{-1})	0.403	0.354	0.357
Unique reflections	9648	9765	14,793
Observed reflections	6130	7384	11,252
Parameters	565	576	1039
R_{int}	0.0458	0.0418	0.0309
R [$I > 2\sigma(I)$]^a	0.0644	0.0588	0.0618
wR [$I > 2\sigma(I)$]^b	0.1268	0.1431	0.1300

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

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

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evaporated *in vacuo* below 50 °C to give a white solid of pseudo-rotaxane named [(H_2**C6N4**)(CB[6])]Cl_2 (1.36 g, 94%). ^{1}H NMR (500 MHz, D_2O, 25 °C): $\delta = 8.65$ (d, $J = 5.7$ Hz, 4H(6)), 7.79(d, $J = 5.9$ Hz, 4H(5)), 5.75 (d, $J = 15.6$ Hz, 12H(c)), 5.60 (s, 12H(b)), 4.49 (s, 4H(4)), 4.32 (d, $J = 5.2$ Hz, 12H(a)), 3.10 (t, $J = 7.4$ Hz, 4H(3)), 0.92 (m, 4H(2)), 0.53 (m, 4H(1)).

Preparation of [(H_2C6N4)(CB[6])](NO_3)$_2$

A pseudo-rotaxane named [(H_2**C6N4**)(CB[6])](NO_3)$_2$ was prepared according to the above procedure just replacing hydrochloric acid with nitric acid.

Preparation of [Cu(H_2C6N4)(CB[6])]$Cl_4\cdot 12H_2O$ (1)

$CuCl_2\cdot 2H_2O$ (37.7 mg, 0.22 mmol) was added to a solution of [(H_2**C6N4**)(CB[6])]Cl_2 (145.5 mg, 0.1 mmol) in 10 ml water. Diffusion of acetone into the reaction mixture in 2 weeks produces light-blue X-ray quality crystals of **1** with an yield of 53%. Anal. Calcd. for $CuC_{54}H_{90}Cl_4N_{28}O_{25}$: C, 37.3; H, 5.2; N, 22.5. Found: C, 37.6; H, 5.1; N, 21.7.

Preparation of [Co(H_2C6N4)(CB[6])]$Cl_4\cdot 14H_2O$ (2)

When a solution of $CoCl_2\cdot 6H_2O$ (52.3 mg, 0.22 mmol) in water was used instead of $CuCl_2\cdot 2H_2O$ in the above procedures for the preparation of polyrotaxane **1**, pink X-ray quality crystals of **2** were obtained by diffusion of acetone into the reaction mixture in 2 weeks (49%). Anal. Calcd. for $CoC_{54}H_{92}Cl_4N_{28}O_{26}$: C, 37.0; H, 5.2; N, 22.4. Found: C, 36.8; H, 4.5; N, 22.1.

Preparation of [Ag(C6N4)(CB[6])]$NO_3\cdot 7H_2O$ (3)

$AgNO_3$ (37.4 mg, 0.22 mmol) was added to a solution of [(H_2**C6N4**)(CB[6])](NO_3)$_2$ (142.1 mg, 0.1 mmol) in 10 ml water. Diffusion of acetone into the reaction mixture in 2 weeks produces colourless X-ray quality crystals of **3** with an yield of 38%. Anal. Calcd. for $AgC_{54}H_{82}N_{29}O_{25}$: C, 41.7; H, 4.6; N, 26.1. Found: C, 41.2; H, 4.8; N, 25.9.

Crystallography

The intensity data for crystals were collected on a Bruker Smart Apex CCD area detector diffractometer at 293 K (**1**, **2**) or 298 K (**3**), using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods with SHELXTL (Bruker, 2000). All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method on F^2. The hydrogen atoms were generated geometrically in **1** and **2**, but in **3**, the hydrogen atoms except for those of water molecules were generated geometrically. Details of the crystal parameters, data collection and refinements for crystals **1**–**3** are summarised in Table 3. Detailed Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC-288678 (**1**), CCDC-288677 (**2**) and CCDC-604939 (**3**).

Supporting information available

X-ray crystallographic file in CIF format, other supporting information data (Tables S1–S2, Figures S1–S3) are available via internet at http://www.informaworld.com/gsch

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