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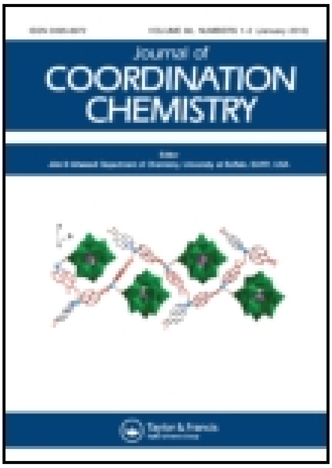

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Syntheses, crystal structures, and magnetic properties of 1-D coordination polymers

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Syntheses, crystal structures, and magnetic properties of 1-D coordination polymers

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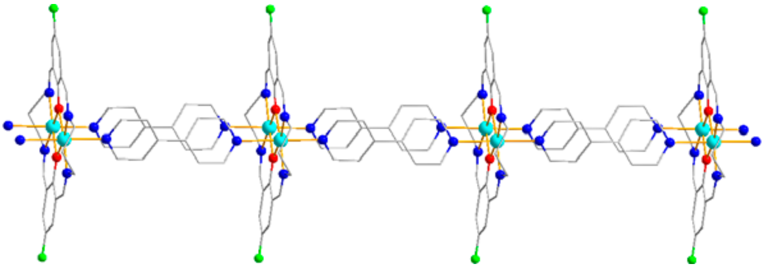

Three novel coordination polymers of Robson-type dinuclear macrocyclic complexes, bridged by 4,4′-bipyridine, were synthesized and fully characterized, Magnetic data reveal that there are strong antiferromagnetic between two Cu(II) ions in the macrocyclic unit and ferromagnetic interaction between the Cu(II) ions in two adjacent macrocyclic units for complexes **1** and **2**.

Three coordination polymers of Robson-type macrocycles, $\{[Cu_4L^1(4,4'\text{-bipy})_2]\cdot 4ClO_4\cdot H_2O\}_\infty$ (**1**), $\{[Cu_4L^2(4,4'\text{-bipy})_4]\cdot 2CH_3CN\cdot 4ClO_4\cdot 2H_2O\}_\infty$ (**2**), and $\{[Zn_2L^2(4,4'\text{-bipy})_2]\cdot (ClO_4)_2\}_\infty$ (**3**) (where H_2L^1 and H_2L^2 are the [2 + 2] condensation products of 1,3-diaminopropane with 2,6-diformyl-4-methylphenol and 2,6-diformyl-4-fluorophenol, respectively), have been synthesized and characterized. Magnetic susceptibility was measured for **1** and **2** from 2 to 300 K. The optimized magnetic data were $J = -368.5\ \text{cm}^{-1}$, $J' = 40.5\ \text{cm}^{-1}$ with $R = 1.69 \times 10^{-6}$ for **1** and $J = -291.22\ \text{cm}^{-1}$, $J' = 83.74\ \text{cm}^{-1}$, $\rho = 0.00168$ with $R = 1.8 \times 10^{-11}$ for **2**, respectively. The data reveal strong antiferromagnetic interactions between two Cu(II) ions in the macrocyclic unit and ferromagnetic interaction between the Cu(II) ions in two adjacent macrocyclic units for **1** and **2**.

Keywords: Robson-type macrocyclic complex; Coordination polymer; Magnetism

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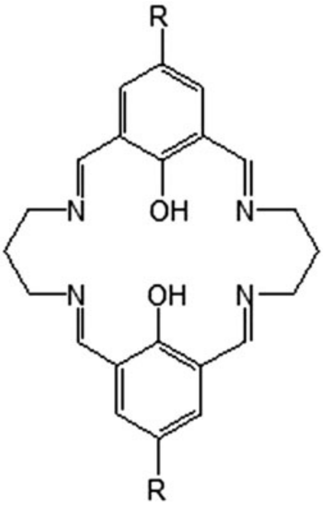
Introduction

Construction of metal–organic frameworks is an active area of materials research [1–6]. Interest is driven by potential applications as functional materials (catalysis, magnetism, gas separation, and nonlinear optics) [7–11] as well as structural diversity and intriguing topologies [12–19]. Crystal engineering depends on understanding and controlling self-assembly. The crystal engineering of coordination frameworks with specific topologies with desired properties remains a challenge, depending on a variety of factors which influence the self-assembly process [20–22]. 4,4′-Bipyridine and its analogs have proved especially useful bridging ligands, resulting in a large number of network structures, including square grid, ribbon, octahedral, diamondoid, and helical frameworks [23–25]. The Champness group demonstrated the use of 4,4′-bipyridine *N*,*N*′-dioxide (bpdo) for preparing coordination polymers with lanthanides [26] and transition metals [27].

Many Robson-type Schiff base macrocyclic complexes were synthesized, and properties such as magnetism and electrochemistry were studied [28–38]. Our group synthesized a series of Robson-type Schiff base macrocyclic complexes and studied magnetism, electrochemical properties, DNA cleavage activity, and SOD activity [39–47]. We recently reported some dimers in which the macrocycles are connected by 4,4′-bipyridine [48, 49]. The Huang Wei group reported the coordination self-assembly of dinuclear Robson-type macrocyclic complexes, but the properties of such coordination polymers have not been studied [50–52]. Bearing these ideas in mind, we designed coordination polymers of Robson-type complexes bridged by 4,4′-bipyridine and find a variety of factors influence the self-assembly process. Our research interest is to investigate the magnetic properties of 4,4′-bipyridine-bridged Robson-type macrocyclic complexes. Herein, we report three new coordination polymers of dinuclear Robson-type macrocyclic complexes. The effect of substituents and diamine types in the macrocycle rings, anions, and metal ions on the final supramolecular assembly is investigated. The structure of the Robson-type macrocyclic ligand is shown in scheme 1.



Scheme 1. Chemical structure of the macrocyclic ligand H_2L, $R = CH_3$, F.

Results and discussion

The complexes were obtained by reaction of 2,6-diformyl-4-R-phenol with 1,3-diaminopropane in the presence of 4,4′-bipy and $M(ClO_4)_2 \cdot 6H_2O$ in acetonitrile–ethanol (V/V, 1 : 1) solution. In the experiment, three kinds of metal salts, $M(OAc)_2$, MCl_2, and $M(ClO_4)_2$, were used to investigate the possibility for the formation of macrocyclic coordination polymers, and we found that **1–3** can be obtained only by using $M(ClO_4)_2$ because of the weak coordination capacity of ClO_4^- compared with those of OAc^- or Cl^-. Moreover, when 1,4-diaminobutane was used to react with 2,6-diformyl-4-R-phenol, we only obtained two tetranuclear complexes, which exhibit wheel-like configuration in which two 4,4′-bipy molecules connect two dinuclear $[M_2L]^{2+}$ units because of spatial hindrance of macrocyclic complexes (where H_2L = macrocycle that is the [2 + 2] condensation product of 2,6-diformyl-4-fluorophenol and 1,4-diaminobutane).

X-ray structure determinations showed that these complexes are 1-D macrocyclic coordination polymers connected by 4,4′-bipy. In IR spectra of the complexes, the sharp C=N stretching bands corresponding to imine groups of the ligand framework are observed at ca. 1638 cm^{-1}, indicating that the macrocyclic complexes have been synthesized. The absorptions of perchlorate are at ca. 1101 cm^{-1} and ca. 631 cm^{-1}. The vibration bands of **1–3** are in agreement with its crystal structure.

The three polymers were characterized by X-ray technology and their crystallographic data, and the details about the data collection are presented in tables 1 and 2.

Crystal structures

The perspective views of **1**–**3** are shown in figures 1–3, respectively.

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

	1	**2**	**3**
Empirical formula	$C_{22}H_{23}ClCuN_4O_6$	$C_{22}H_{20}ClCuFN_{4.50}O_{5.25}$	$C_{21}H_{18}FN_4O_5ZnCl$
(Formula weight)	538.43	549.42	526.21
Crystal system, space group	Monoclinic, *C2/c*	Monoclinic, *C2/c*	Monoclinic, *C2/c*
a, b, c [Å]	20.835(4), 11.531(2), 20.278(4)	25.55(1), 12.15(5), 20.49(1)	20.043(1), 11.772(9), 20.172(1)
α, β, γ [°]	90, 110, 90	90, 127, 90	90, 115, 90
Volume [$Å^3$]	4573.2(1)	5069(5)	4296.6(6)
Z, *D* (Calcd) [g/cm^3]	8, 1.564	2, 1.452	8, 1.627
μ (Mo Kα) [/mm], *F* (0 0 0)	1.119, 2216	1.017, 2264	1.319, 2144
Crystal size [mm]	0.20 × 0.22 × 0.26	0.22 × 0.24 × 0.30	0.20 × 0.22 × 0.26
Temp., [K]	291	291	291
Mo Kα radiation [Å]	0.71073	0.71073	0.71073
θ Range [°]	2.1, 26.0	2.0, 26.0	2.1, 26.0
Data-set	−25 : 24; −14 : 14; −12 : 24	−28 : 31; −14 : 12; −25 : 25	−24 : 17; −14 : 14; −24 : 24
Tot., uniq. data *R*(int)	12,656, 4462, 0.036	14,192, 4973, 0.055	12,232, 4221, 0.042
Observed data [$I > 2.0\ \sigma(I)$]	3388	3161	3266
Nref, Npar	4462, 323	4973, 335	4221, 298
R, wR_2, *S*	0.0563, 0.1405, 1.06	0.0582, 0.1371, 1.06	0.0454, 0.1016, 1.05
Max. and Av. shift/error	0.00, 0.00	0.00, 0.00	0.00, 0.00
Min. and Max. Resd. Dens. [$e/Å^3$]	−0.41, 0.26	−0.56, 0.62	−0.60, 0.30

Table 2. Selected bond distances (Å) and angles (°) for **1**–**3**.

1		**2**		**3**	
Bond lengths (Å)		Bond lengths (Å)		Bond lengths (Å)	
Cu1–O1	1.964(3)	Cu1–O1	1.976(3)	Zn1–O1	2.073(2)
Cu1–N1	2.434(4)	Cu1–O1c	1.979(4)	Zn1–N1	2.269(2)
Cu1–N2	2.421(4)	Cu1–N1	2.401(4)	Zn1–N3	2.044(3)
Cu1–N3	1.978(4)	Cu1–N2a	2.703(4)	Zn1–N4	2.060(3)
Cu1–N4	1.987(3)	Cu1–N3	1.968(5)	Zn1–N2b	2.405(2)
Cu1–O1c	1.976(3)	Cu1–N4	1.953(4)	Zn1–O1c	2.058(2)
Bond angles (°)		Bond angles (°)		Bond angles (°)	
O1–Cu1–N1	90.89(1)	O1–Cu1–N1	95.85(1)	O1–Zn1–N1	94.46(1)
O1–Cu1–N2	97.44(1)	O1–Cu1–N3	91.82(1)	O1–Zn1–N3	89.51(1)
O1–Cu1–N3	91.95(1)	O1–Cu1–N4	169.25(1)	O1–Zn1–N4	169.43(1)
O1–Cu1–N4	169.96(1)	O1–Cu1–N2a	92.47(1)	O1–Zn1–N2b	90.32(9)
O1–Cu1–O1c	77.57(1)	O1–Cu1–O1c	77.01(1)	O1–Zn1–O1c	79.62(8)
N1–Cu1–N2	169.13(1)	N1–Cu1–N3	88.90(1)	N1–Zn1–N3	89.29(1)
N1–Cu1–N3	82.15(1)	N1–Cu1–N4	88.76(1)	N1–Zn1–N4	89.56(1)
N1–Cu1–N4	85.16(1)	N1–Cu1–N2a	170.54(1)	N1–Zn1–N2b	174.38(1)
O1c–Cu1–N1	90.03(1)	O1c–Cu1–N1	94.78(1)	O1c–Zn1–N1	92.55(1)
N2–Cu1–N3	90.55(1)	N3–Cu1–N4	97.99(1)	N3–Zn1–N4	100.32(1)
N2–Cu1–N4	87.71(1)	N2a–Cu1–N3	86.32(1)	N2b–Zn1–N3	87.80(1)
O1c–Cu1–N2	98.56(1)	O1c–Cu1–N3	168.53(1)	O1c–Zn1–N3	169.08(1)
N3–Cu1–N4	96.63(1)	N2a–Cu1–N4	83.83(1)	N2b–Zn1–N4	86.23(9)
O1c–Cu1–N3	166.87(1)	O1c–Cu1–N4	92.96(1)	O1c–Zn1–N4	90.45(1)
O1c–Cu1–N4	93.18(1)	O1c–Cu1–N2a	91.48(1)	O1c–Zn1–N2b	91.22(9)

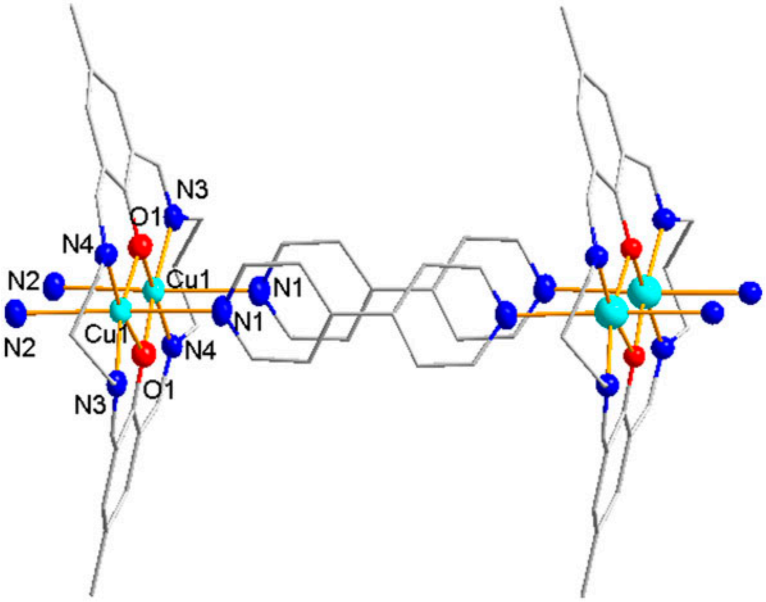


Figure 1. Perspective view of the macrocyclic unit of **1**; hydrogens have been omitted for clarity (ellipsoids are drawn at 30% probability).

$\{[Cu_4L^1(4,4'\text{-bipy})_2]\cdot 4ClO_4\cdot H_2O\}_\infty$ (1). X-ray structure determination showed that **1** has an infinite 1-D molecular ladder motif composed of macrocyclic dinuclear copper complex with 4,4′-bipyridine molecules. There is a C_2 axis in the molecular structure of **1**, in the

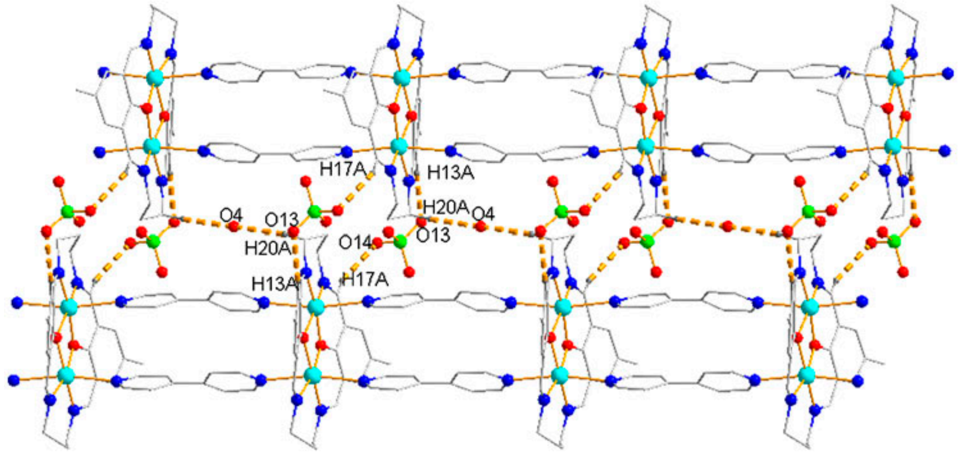


Figure 2. View of the 2-D network depicting the connection via C–H···O hydrogen bonds in **1**.

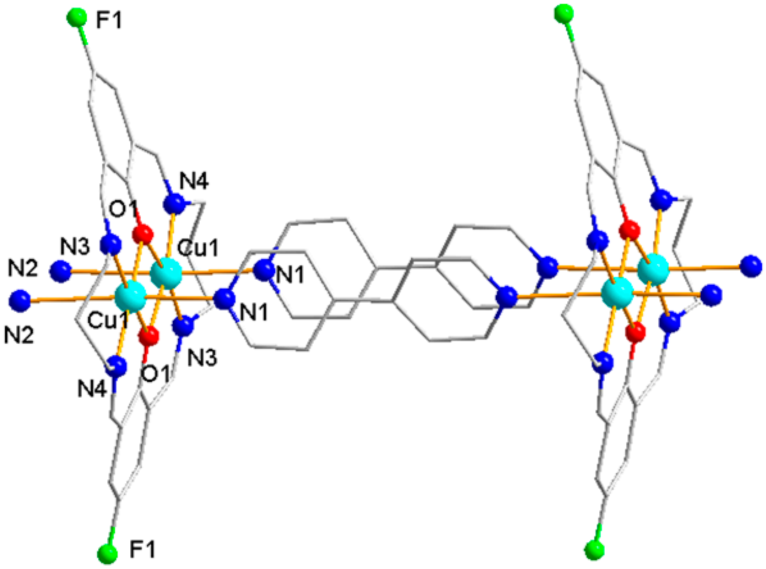


Figure 3. Perspective view of the macrocyclic unit of **2**; hydrogens have been omitted for clarity (ellipsoids are drawn at 30% probability).

middle of the line Cu1–Cu1 and perpendicular to the plane comprised of two copper(II) ions and two phenoxides. The coordination polyhedron of each copper(II) can be described as octahedral. The basal coordination plane is composed of two imine nitrogens and two phenoxides, where the phenoxides bridge two copper(II) ions. The apical positions are occupied by two nitrogens from two 4,4′-bipyridine molecules with the Cu–N distances of 2.421 Å, where the two 4,4′-bipyridine molecules locate on opposite sides of the macrocycle. The Cu–N and Cu–O distances in the basal plane are 1.964–1.987 Å. The copper–copper separation (3.123(6) Å) and phenoxide oxygen bridged angle (103.65(1)°) are comparable with those found in analog [49].

The stacking diagram along the *c*-axis of **1** is shown in figure 2. The complex is a 1-D chain polymer in which macrocycles are connected by 4,4′-bipyridine molecules. The chain structure is formed from the macrocyclic structure holding two metal ions together by 4,4′-bipyridine molecules through coordination.

The distance between Cu(II) ions in one macrocyclic unit is 3.06 Å, while the distance between Cu(II) ions bridged by 4,4′-bipy is 11.53 Å. The pyridine ring planes in two 4,4′-bipy are parallel to their counterparts with centroid–centroid distance of 3.59 Å, indicating that there are strong π–π stacking interactions between two 4,4′-bipy blocks.

Hydrogen bond interactions play an important role in maintaining the 2-D network of **1**. As shown in figure 2, each perchlorate acts as H-bonding acceptor to link 1-D chain units through the following hydrogen bond interactions: C17–H17A···O14, C13–H13···O13, C20–H20A···O4 (having H···O distances 2.531, 2.561, 2.539 Å and C–H···O angles 151.83°, 169.26°, 171.09°, respectively).

$\{[Cu_4L^2(4,4'\text{-bipy})_4]\cdot 2CH_3CN\cdot 4ClO_4\cdot 2H_2O\}_\infty$ (2). Complex **2** is obtained in the same procedure as **1**, except that fluoro substituent in benzene ring was used instead of methyl. The crystal structure of **2** (figure 3) is similar to that of **1**, involving a C_2 axis of the same position and orientation with the one in **1**. The distances of 1.953–1.979 Å between Cu and coordination atoms in the basal plane of **2** are shorter than those of **1** and the apical Cu–N distances are 2.401 and 2.703 Å, respectively. The distance of 3.09 Å between the Cu(II) ions in one macrocyclic unit and the distance of 12.15 Å between the Cu(II) ions bridged by 4,4′-bipy are bigger than those of **1**. The copper–copper separation (3.0925(2) Å) and phenoxide oxygen bridged angle (102.86(1)°) are comparable with those found in an analog [41].

Each fluoro is a H-bond acceptor to link 1-D chains through the following hydrogen bond interaction (figure 4): C1–H1···F1 (having H···F distances 2.524 Å and C–H···F angles 135.57°).

$\{[Zn_2L^2(4,4'\text{-bipy})_2]\cdot(ClO_4)_2\}_\infty$ (3). Complex **3** is obtained in the same procedure as the one in **2**, except that zinc ions were used instead of copper ions. The crystal structure of **3** (figure 5) is similar to that of **2**. The distances of 2.044–2.073 Å between Zn and coordination atoms in the basal plane of **3** are bigger than those of **2** and the apical Zn–N distances, 2.269 and 2.405 Å, are shorter than those of **2**.

Similar to those of **2**, each fluoro is a H-bond acceptor linking 1-D chains through the following hydrogen bond interaction (figure 6): C18–H18···F1 (having H···F distances 2.527 Å and C–H···F angles 121.59°).

Magnetic properties

The temperature dependences of the magnetic susceptibility data for **1** and **2**, in the form of χ_m and $\chi_m T$, are shown in figures 7 and 8. The overall appearance of the figures is indicative of strong antiferromagnetic interactions. Taking into account that the Cu–Cu distances in the macrocyclic rings (3.063 Å for **1** and 3.093 Å for **2**) are shorter than those of adjacent macrocyclic rings (11.531 Å for **1** and 12.152 Å for **2**), the exchange interactions of Cu–Cu in each macrocyclic unit are stronger than those of Cu–Cu between macrocyclic units. The magnetic susceptibility for such a model system can be analyzed by using the Heisenberg

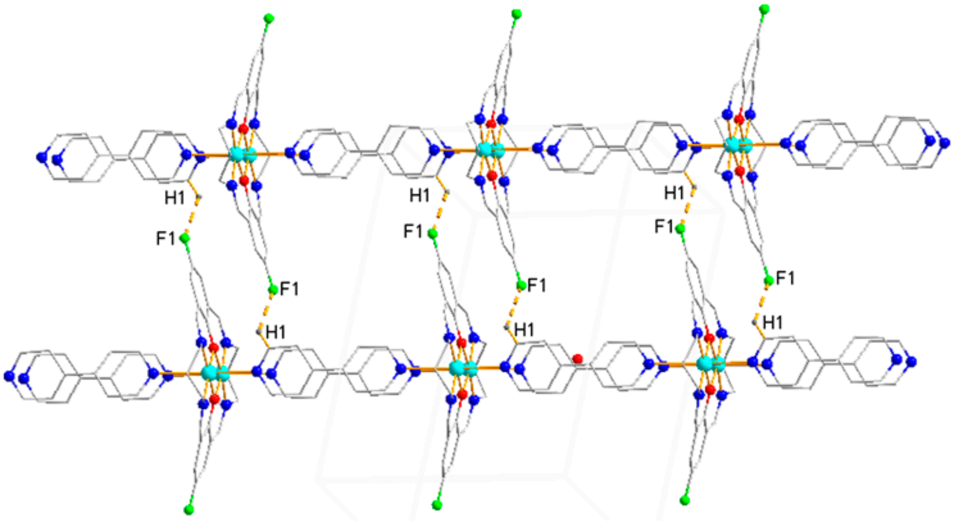


Figure 4. View of the 2-D network depicting the connection via C–H···F hydrogen bonds in **2**.

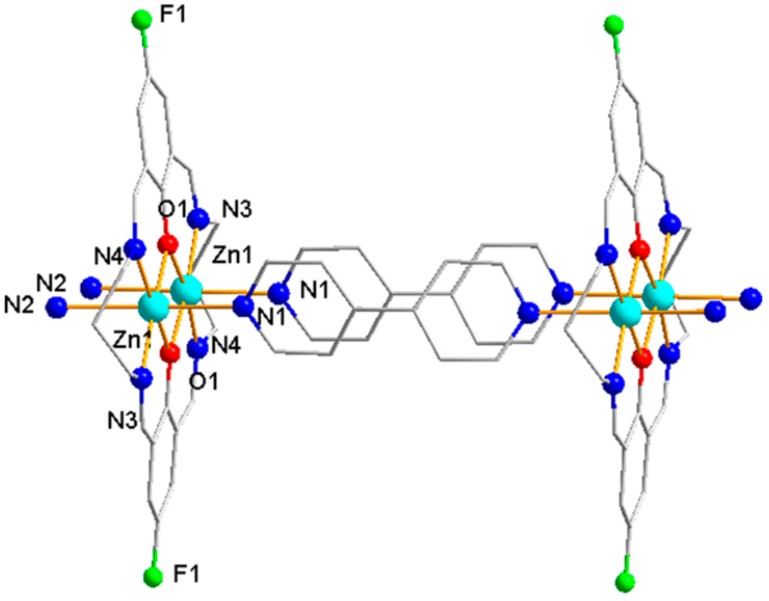


Figure 5. Perspective view of the macrocyclic unit of **3**; hydrogens have been omitted for clarity (ellipsoids are drawn at 30% probability).

model for the dinuclear copper(II) complex with consideration of the interactions between molecules [53, 54]. The magnetic susceptibility data were analyzed for **1** and **2** on the basis of equation (1), where the values of N, g, β, k, ρ, and T have usual meanings, z is the number of nearest neighboring Cu(II) centers (in the two complexes $z = 4$), and J' accounts for

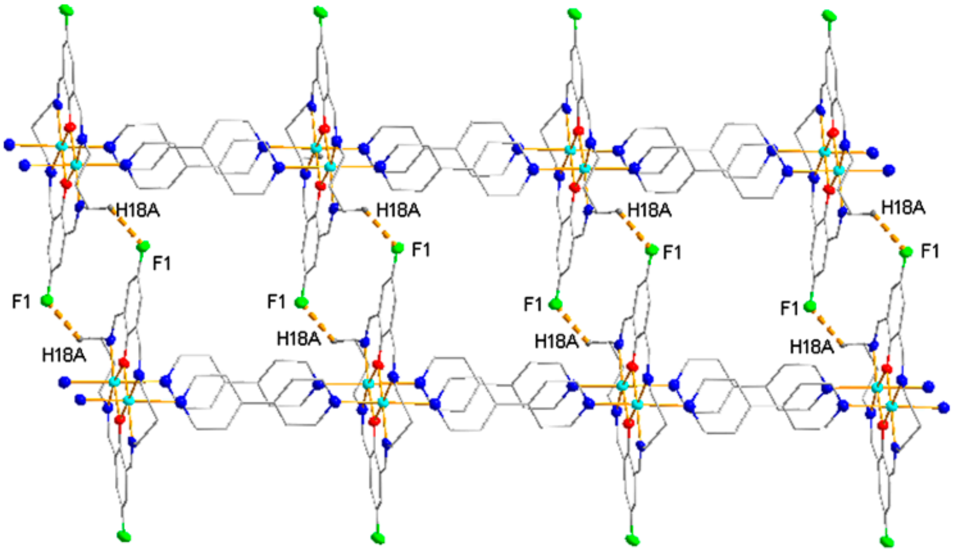


Figure 6. View of the 2-D network depicting the connection via C–H···F hydrogen bonds in **3**.

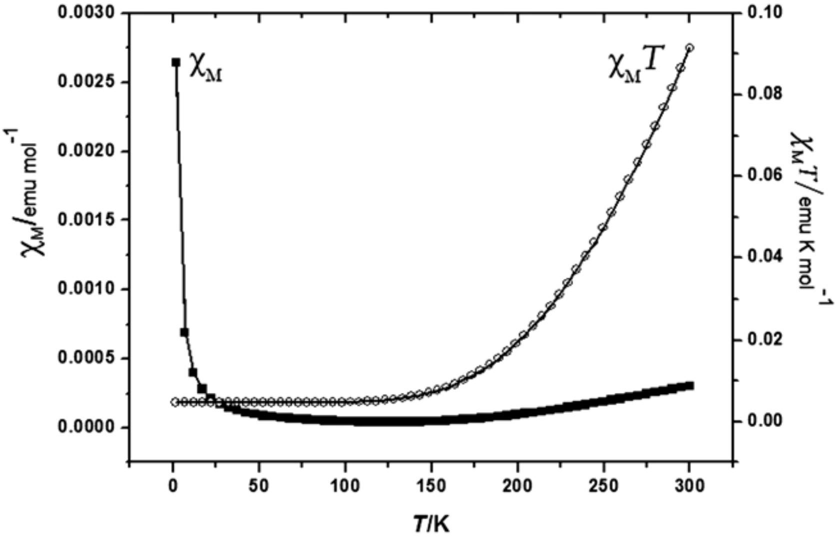


Figure 7. Plots of χ_m(■) and χ_mT (○) *vs.* temperature for **1**, where the solid line represents the best fit curve.

the presence of magnetic interactions between neighboring dinuclear units. An excellent fit was obtained which gave the parameters $g = 2.0$, $J = -368.5\ \text{cm}^{-1}$, $J' = 40.5\ \text{cm}^{-1}$, $\rho = 0.00633$ with $R = 1.69 \times 10^{-6}$ for **1** and $g = 2.2$, $J = -291.22\ \text{cm}^{-1}$, $J' = 83.74\ \text{cm}^{-1}$, $\rho = 0.00168$ with $R = 1.8 \times 10^{-11}$ for **2**. The values of J for **1** and **2** are smaller than those of similar macrocyclic complexes, but the J' is significantly larger than those of other complexes [41, 49].

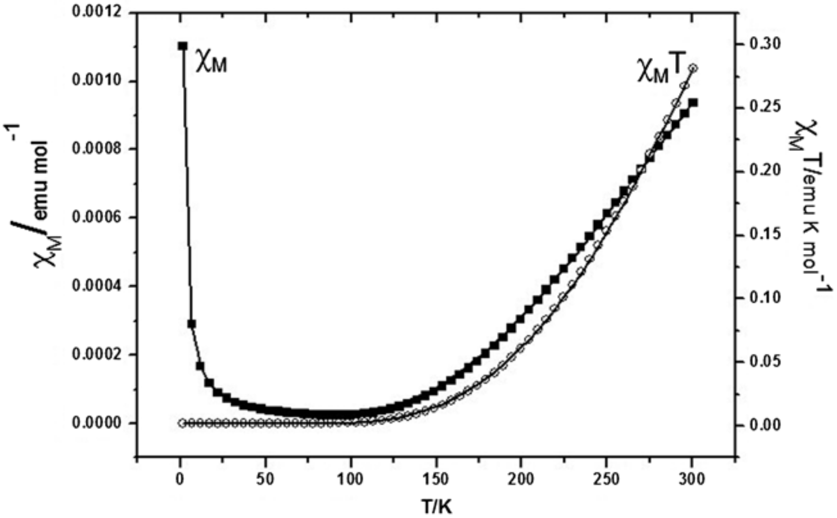


Figure 8. Plots of χ_m(■) and χ_mT (○) *vs.* temperature for **2**, where the solid line represents the best fit curve.

$$\chi = \frac{2Ng^2\beta^2}{kT} \times \frac{1}{3 + e^{-2J/kT}}$$

$$\chi_M = \frac{\chi}{1 - (2zJ'/Ng^2\beta^2)\chi}(1-\rho) + \rho \times \frac{Ng^2\beta^2}{2KT} \qquad (1)$$

Crawford reported that the magnetic behavior of a bis(hydroxyl)-bridged dicopper complex changes from antiferromagnetic to ferromagnetic at the crossover point of Cu–O–Cu angle of 97.50° [55]. The magnetic interaction of copper ions in the macrocyclic units with the Cu–O–Cu angle 102.05° for **1** and 102.87° for **2** is in agreement with the trend. The larger *J*′ in the complex, assigned to the interactions between two macrocyclic units, reveals that the bis-bipy-bridged groups can act as a magnetic exchange pathway. Han Woong Park [56] reported that the bond length of the C–C bond connecting two pyridine rings in 4,4′-bipy can influence the magnetic interactions. Although the pyridine ring planes in one 4,4′-bipy molecule are not coplanar (dihedral angle of 38.22° and 33.27° for **1** and **2**, respectively), the C–C bonds in **1** and **2** (the bond length of C3–C8 is 1.423 Å for **1** and 1.468 Å for **2**) have double bond character, which keep the conjugation of the 4,4′-bipy molecules, increasing the magnetic interactions.

Conclusion

Three 1-D macrocyclic dinuclear coordination polymers, with 4,4′-bipy bridging between two macrocyclic units, were prepared and structurally characterized. The 1-D single-stranded chain structure is independent of counter anions and diamine type in macrocyclic rings. H-bond formation is the other factor for construction of the final supramolecular networks. H-bond involving perchlorates in **1**, fluoro in **2** and **3** play an important role in maintaining 2-D structures. The magnetic measurement of **1** and **2** revealed that 4,4′-bipy can serve as an effective magnetic pathway, resulting in ferromagnetic interaction between Cu(II) ions in two adjacent macrocyclic units.

Experimental setup

All solvents and chemicals were of analytical grade and used as received, except ethanol that was purified to absolute by the general method. IR spectra were recorded on a Vector 22 FT-IR spectrophotometer using KBr disks. Elemental analyses were performed on a Perkin-Elmer 240 analyzer. Magnetic susceptibility of a crystalline-powdered sample was measured on a SQUID-based sample magnetometer from 2.0 to 300 K, and the diamagnetic corrections were made according to Pascal's constants.

Crystal structure determination

Crystals were measured on a Bruker AXS SMART diffractometer (Mo Kα radiation monochromator). Data reduction and cell refinement were performed by SMART and SAINT [57]. The structures were solved by direct methods (Bruker SHELXTL) and refined on F^2 by full-matrix least squares (Bruker SHELXTL) using all unique data [58]. The non-H atoms in the structure were treated as anisotropic. Hydrogens were located geometrically and refined in riding mode.

Preparation of complexes

$\{[Cu_4L^1(4,4'\text{-bipy})_2]\cdot 4ClO_4\cdot H_2O\}_\infty$ (1). To a mixture of acetonitrile–ethanol (1 : 1, 40 mL) containing 2,6-diformyl-4-methylphenol (0.082 g, 0.5 mM) and $Cu(ClO_4)_2\cdot 6H_2O$ (0.186 g, 0.5 mM), four drops of triethylamine was added. After a while, 1,3-diaminopropane (0.037 g, 0.5 mM) in acetonitrile–ethanol (1 : 1, 10 mL) was slowly added. The mixture was stirred for 4 h, then 4,4′-bipy (0.312 g, 2 mM) in acetonitrile–ethanol (1 : 1, 10 mL) was introduced. The mixture was refluxed for 1 h, then cooled to room temperature and filtered. Green crystals of **1** were obtained by vapor diffusion of diethyl ether into the solution of the complex in acetonitrile–ethanol. Yield: 0.26 g, 63%. Anal. Calcd for $C_{22}H_{23}ClCuN_4O_6$: C, 49.07; H, 4.30; N, 10.40. Found: C, 48.88; H, 4.21; N, 10.57. IR (KBr, ν/cm^{-1}): 1638($\nu_{C=N}$), 1101(ν_{ClO4^-}), 639(δ_{ClO4^-}).

$\{[Cu_4L^2(4,4'\text{-bipy})_4]\cdot 2CH_3CN\cdot 4ClO_4\cdot 2H_2O\}_\infty$ (2). Complex **2** was obtained in a manner similar to that used for **1**, except that 2,6-diformyl-4-fluorophenol was used instead of 2,6-diformyl-4-methylphenol. Yield: 0.136 g, 29%. Anal. Calcd for $C_{22}H_{20}ClCuFN_{4.50}O_{5.25}$: C, 48.09; H, 3.67; N, 11.47. Found: C, 47.62; H, 3.79; N, 11.43. IR (KBr, ν/cm^{-1}): 3055, 2918 (C–H), 1638($\nu_{C=N}$), 1079(ν_{ClO4^-}), 631(δ_{ClO4^-}).

{[Zn_2L^2(4,4′-bipy)$_2$]·2ClO_4}$_\infty$ (3). Complex **3** was obtained in a manner similar to that used in **2**, except that $Zn(ClO_4)_2 \cdot 6H_2O$ was used instead of $Cu(ClO_4)_2 \cdot 6H_2O$. Yield: 0.095 g, 21%. Anal. Calcd for $C_{21}H_{18}FN_4O_5ZnCl$: C, 48.89; H, 3.48; N, 11.16. Found: C, 48.91; H, 3.41; N, 11.31. IR (KBr, cm^{-1}): 1639($\nu_{C=N}$), 1103($\nu_{ClO_4^-}$), 645($\delta_{ClO_4^-}$).

Caution! Although no problems were encountered in this work, the perchlorate salt is potentially explosive. It should be prepared in small quantities and handled with care.

Supplementary material

CCDC 837666, CCDC 837665 and CCDC 837667 contain the supplementary crystallographic data for **1**, **2**, and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223 336 033; or E-mail: deposit@ccdc.cam.ac.uk.

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