Macrocyclic, Dinuclear Zinc(II)-Directed Self-Assembly with Pyridine, 2,2′-Bipyridine and 2-Methylquinoline: μ^2-OH Bridging Bi-Macrocyclic Complexes and Hydrogen-Bond-Supported Donor-Acceptor Complexes

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Two macrocyclic dinuclear zinc(II) complexes (**1a** and **1b**) have been self-assembled in the presence of pyridine and 2,2′-bipyridine, respectively, to form μ^2-OH-bridged bimacrocycles with a Zn_4O_4 cavity through coordination bonding. The X-ray structural analysis reveals that both compounds {**2a**: $[Zn_4L^a{}_2(OH)_2]_2(ClO_4)_2$; **2b**: $[Zn_4L^b{}_2(OH)_2]_2(ClO_4)_2$} have an open-mouthed sandwich-like structure with π–π interactions between parts of two phenyl rings to strengthen two hydroxyl groups connecting the metal atoms in the same direction of the macrocycle. Furthermore, nonclassical C–H···Cl intermolecular interactions have been observed in the crystal of **2b**. In addition, the reaction of **1a** with quinoline derivatives has yielded novel hydrogen-bond-supported donor-acceptor complexes {**3a**: $[Zn_2L^a(H_2O)_2(C_{10}H_9N)_2](ClO_4)_2$}. The crystallographic study of the complex containing 2-methylquinoline indicates that two 2-methylquinoline molecules are linked to two coordinating water molecules above and below the macrocyclic framework through O–H···N hydrogen bonds. The 2-methylquinoline plane interacts in a face-to-face fashion with the phenyl ring of adjacent macrocyclic frameworks, forming an ordered arrangement where one macrocycle and two 2-methylquinolines are arrayed alternately with almost the same separation. The interplanar distance mentioned before is ca. 3.6 Å.

Introduction

Metal-directed self-assembly has been actively investigated in recent years because such a phenomenon offers a new and effective way for the construction of organized structures. The known application of this category of self-assembly is mainly focused on the combination of naked or decorated mononuclear metal species with well-designed organic ligands, leading to the production of metal-ligand frameworks with specific structural topologies.[1] Self-assembly involving dinuclear macrocyclic components has rarely been reported[2] since the first homodinuclear macrocyclic complexes were synthesized by template condensation in the early 1970s and a subsequent systematic study of their modeling of metallobiosites.[3]

The coordination behavior of the metal atoms in these complexes plays a key role in controlling the assembly pattern: metal ions with a defined coordination geometry (e.g. square planar, tetrahedral, pyramidal, and octahedral configurations) have to be specifically chosen and/or deliberately modified as building blocks to realize the anticipated assembly; the effect of noncovalent interactions such as hydrogen bonding, aromatic π−π stacking and charge-transfer interactions should also be taken into account.[4]

We recently reported two infinite molecular ladder polymers composed of a macrocyclic component (**1**) (Scheme 1) with 4,4′-bipyridine, in which two adjacent zinc(II) ions, pre-positioned in the macrocyclic backbone, have been linked by 4,4′-bipyridine ligands via coordinating bonds, together with the change of the coordination configuration of the metal atom from a five-coordinate pyramid to a six-coordinate octahedron (Scheme 2, a).[5] To further study the effect of the dinuclear zinc(II) macrocyclic component in self-assembly, some other mono- and bifunctional aromatic ligands have been utilized instead of 4,4′-bipyridine with the expectation of obtaining a novel type of supramolecular compounds or coordination polymers with special structural topologies. When 4-aminopyridine or pyridine-4-carboxylic acid is allowed to react with **1**, molecular ladder elements are obtained (Scheme 2, b and c).[6] We report here two kinds of new complexes obtained by the reaction of macrocyclic component **1** with pyridine, 2,2′-pyridine and quinoline derivatives. Unlike the reaction with 4,4′-bipyrid-

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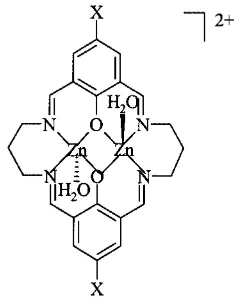
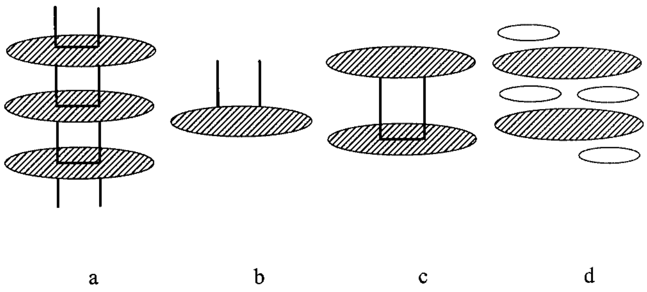
ine (1-D molecular ladder polymers bridged by M−N coordinating bonds), sandwich-like structures (**2**) are formed where **1** moieties are connected by two μ²-OH groups via bridging zinc atoms in the presence of pyridine or 2,2′-bipyridine ligands (Scheme 2, c). When a quinoline derivative is involved, an infinite one-dimensional hydrogen-bond-supported donor-acceptor polymer is obtained where no coordinating interaction exists between layers (Scheme 2, d).



$[Zn_2L(H_2O)_2]^{2+}$ (**1**) L^a: X = Me, L^b: X = Cl

Scheme 1. Macrocyclic units **1** used as building blocks

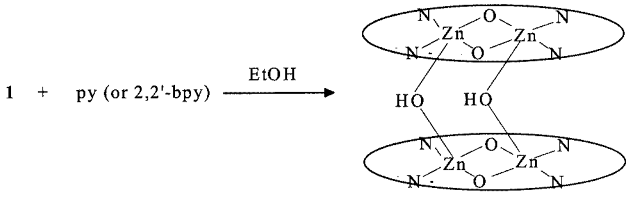


Scheme 2. (a) A molecular ladder with macrocyclic platforms; (b) a molecular ladder element with a macrocyclic base; (c) a wheel-like structural unit; (d) a donor-π-acceptor structural pattern

Results and Discussion

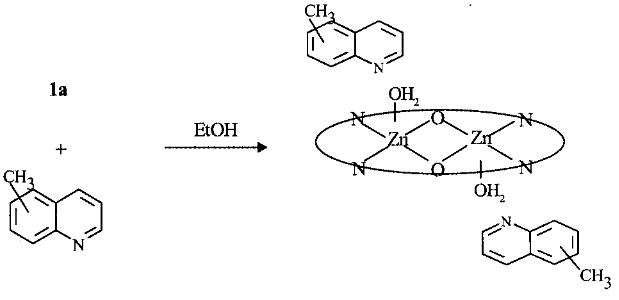
Preparations and Characterization

The syntheses of **2a** and **2b** and **3a** and **3b** are shown in Schemes 3 and 4, respectively. The preparation is a simple one-step reaction that gives the products in high yields. In the process of preparing **2**, however, we were surprised to find that irrespective of whether pyridine or 2,2′-pyridine was used, the same products were obtained (spectral characterization and microanalyses). It seems that pyridine and 2,2′-pyridine serve as bases in the formation of **2a** and **2b**, and that these bases are necessary to assist hydrolysis at the zinc(II) cations, which acts as a Lewis acid under the conditions of the experiments.



2a, 2b

Scheme 3. Synthesis of complexes **2a** and **2b**



3a, 3b

Scheme 4. Synthesis of compounds **3a** and **3b**

Related infrared and mass spectroscopic data of all compounds indicate the existence of macrocyclic skeletons together with perchlorate anions. In addition, strong broad bands for the O−H stretching vibration of the bridging hydroxyl groups are observed at 3512 cm^{-1} for **2a** and 3533 cm^{-1} for **2b**. The hydrogen atoms belonging to the macrocyclic rings are also observed in the ^{1}H NMR spectra of **2a** and **2b**, although the nature of the self-assembly products can only be clearly determined from the ^{1}H NMR spectra of **3a** and **3b**, which demonstrate the presence of hydrogen atoms linking to quinoline rings apart from the macrocycle. However, this routine spectroscopic analysis could not provide the detailed information necessary to determine the structures of the products here.

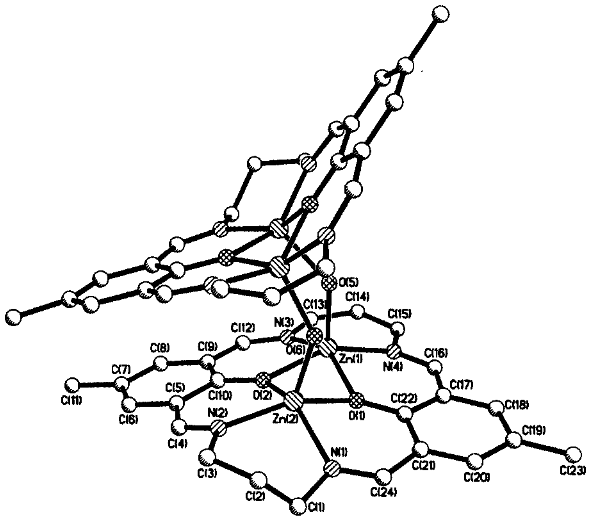
Structural Description of $\{[Zn_4L^a{}_2(OH)_2]_2(ClO_4)_2(H_2O)_2CH_3OH\}$ (2a) and $\{[Zn_4L^b{}_2(OH)_2](ClO_4)_2(H_2O)_2C_2H_5OH\}$ (2b)

The X-ray structural analysis of **2a** and **2b** shows that both compounds have a unique open-mouthed sandwich-like structure consisting of two macrocyclic covers with two bridging OH groups in the middle (Figure 1). There are two crystallographically independent $[Zn_4L^a{}_2(OH)_2]^{2+}$ (see Scheme 1) ions per asymmetric unit in **2a** with one methanol, two water molecules, and four perchlorate anions noncoordinating. The structure of **2b** has only one crystallographically independent $[Zn_4L^b{}_2(OH)_2]^{2+}$ moiety in the asymmetric cell; one ethanol, two water molecules as well as two perchlorate anions are free from coordination and located in the lattice. The change of the substituted functional group leads to a modification of the crystal system and space group from monoclinic (*P*21/*c*) in **2a** to triclinic

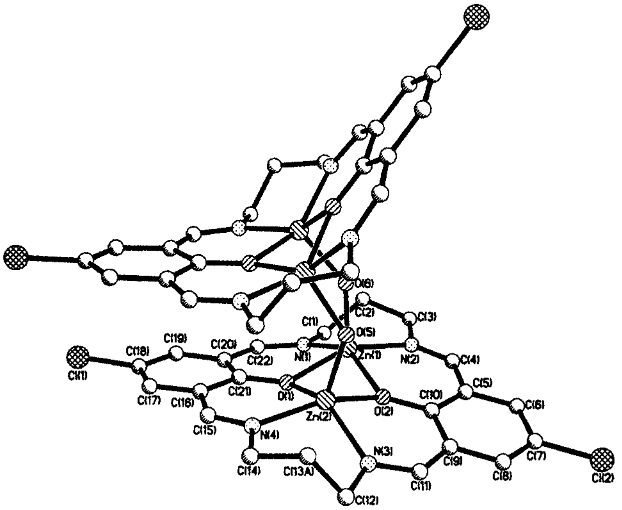
($P\bar{1}$) in **2b**. In complexes **2a** and **2b**, all metal atoms have similar pyramidal configurations where each zinc(II) atom is situated slightly above the base plane composed of two imine nitrogen atoms and two phenolic oxygen atoms, with the axial position occupied by one OH group. Each macrocyclic framework is folded to fit the requirement of two Zn−OH−Zn bond angles [**2a**: 133.6(3)°, 137.8(3)°; **2b**: 133.3(3)°, 141.8(3)°]. In each subunit of one molecule, one part of one ring is nearly parallel to its counterpart in the other one (with a dihedral angle of 9.1° in **2a** and 0.2° in **2b**), while the other parts of the two rings are bent in the opposite position to a certain degree (with a dihedral angle of 42.8° in **2a** and 56.5° in **2b**). The geometric data of the two compounds with respect to the hydroxyl groups are given in Table 1; the average Zn−O (bridging OH) distances are 1.946 Å for **2a** and 1.933 Å for **2b**.

Although the two compounds have similar molecular structures, they have different packing in their crystals (Figure 2) because of the different substituted groups in their macrocyclic backbones. In **2a** there seems to be no intermolecular interactions, whereas in the crystal structure of **2b**, two adjacent chlorine atoms on benzene rings of two different macrocyclic frameworks and their α-positioned hydrogen atoms in phenyl rings are involved in nonclassical C−H···Cl intermolecular interactions in an end-to-end fashion. Thus a 1-D chain structure is formed with the assistance of eight-membered ring structures containing two C−H···Cl H-bonds. There have been a few reports on C−H···X hydrogen bonds in organic and organometallic compounds (where X can be covalently bound atoms or anions),[7] but whether chlorine atoms can be H-bonding acceptors or not is still controversial.[8] Alhough the existence of C−H···Cl hydrogen bonds is questioned, a statistical survey on more than one hundred crystal structures containing structural patterns similar to that in **2b** showed that this kind of intermolecular interaction is not uncommon, and molecular orbital calculations on the energetics of this structural pattern supported the qualitative observation as well.[9] The length of the C−H···Cl intermolecular interactions in our compound agrees well with those reported previously, except that the intermolecular Cl···Cl distances are slightly longer.[10] Thus it is proposed that the different packing in **2a** and **2b** arises from the different substituted groups on the phenyl rings.

It is interesting to observe that each structure shows a rectangular Zn_4 array containing a rigid Zn_4O_4 cavity in both compounds (Figure 3). This arrangement is similar to that reported by Asato et. al in which a tetranuclear zinc(II) complex was synthesized by a template condensation.[11] The related geometric data are listed in Table 2. The cavity is so small that neither solvent molecules nor perchlorate anions can be hosted. In contrast to the situation with 4,4′-bipyridine, pyridine ligands could not be bound to the zinc(II) atoms on the macrocyclic platform to yield a six-coordinate geometry via π−π interactions of the pyridine rings. The reason for this may be that single Zn−N(pyridine) bonds would be freely rotating and therefore they could not be fixed onto the macrocycle due to the spatial repulsion.



2a



2b

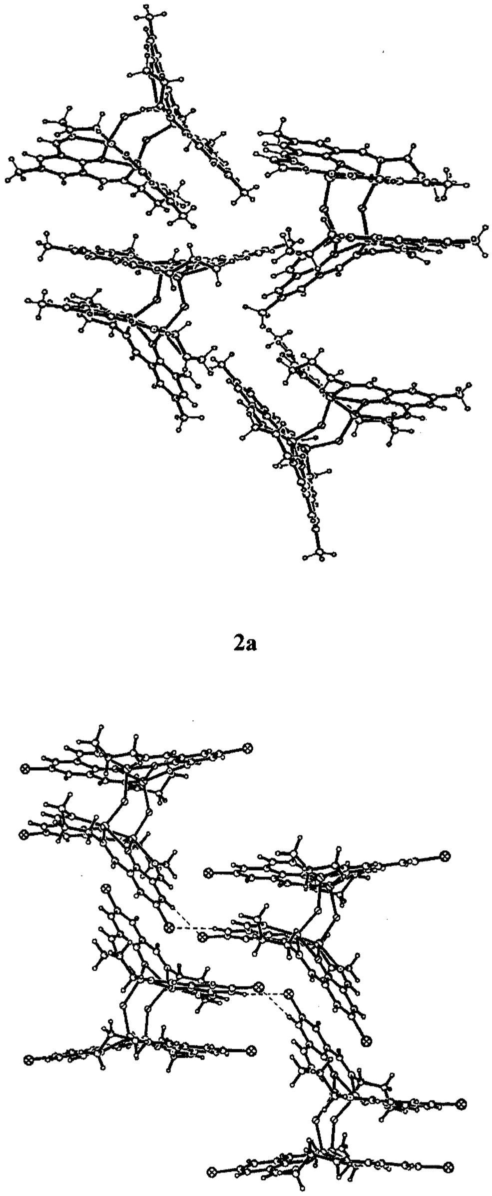
Figure 1. Ball-and-stick representation of the structures of complex cations from **2a** and **2b**; only one of the two tetranuclear clusters from **2a** is shown as they are very similar

This means that monofunctional aromatic ligands cannot take the place of the 4,4′-bipyridine ligands, which are framed with the assistance of the macrocyclic skeleton. It is likely that the absence of 2,2′-bipyridine from the macrocyclic framework is also due to the steric hindrance between aromatic rings. Therefore, in the above two cases, small-sized hydroxyl groups from the solution function as bridges to link two macrocyclic species by coordinating to zinc(II) atoms. Regarding the five-coordinate geometry of zinc(II) atoms in **2**, our prior and current research[2,12] indicates that five-coordinate configuration is preferred if linear monofunctional or bifunctional nonaromatic ligands are used. However, unlike **2**, these nonaromatic ligands will occupy the axial position of the pyramid around the two zinc(II)

Table 1. Selected bond lengths [Å] and angles [°] in **2a** and **2b**; only those associated with bridging OH groups are listed

2a			
Zn(1)−O(5)	1.961(5)	Zn(2)−O(6)	1.925(6)
Zn(3)−O(5)	1.948(5)	Zn(4)−O(6)	1.964(6)
Zn(5)−O(11)	1.933(5)	Zn(6)−O(12)	1.933(6)
Zn(7)−O(11)	1.928(5)	Zn(8)−O(12)	1.934(6)
O(5)−Zn(1)−N(3)	109.6(3)	O(5)−Zn(1)−N(4)	105.9(3)
O(5)−Zn(1)−O(1)	100.7(2)	O(5)−Zn(1)−O(2)	97.1(2)
O(6)−Zn(2)−N(1)	107.2(3)	O(6)−Zn(2)−N(2)	111.5(3)
O(6)−Zn(2)−O(1)	96.7(2)	O(6)−Zn(2)−O(2)	110.6(2)
O(5)−Zn(3)−N(7)	114.9(3)	O(5)−Zn(3)−N(8)	106.2(3)
O(5)−Zn(3)−O(3)	93.9(2)	O(5)−Zn(3)−O(4)	105.6(2)
O(6)−Zn(4)−N(5)	107.0(3)	O(6)−Zn(4)−N(6)	110.3(4)
O(6)−Zn(4)−O(3)	107.5(2)	O(6)−Zn(4)−O(4)	98.2(2)
O(11)−Zn(5)−N(9)	101.2(2)	O(11)−Zn(5)−N(10)	112.5(2)
O(11)−Zn(5)−O(7)	96.9(2)	O(11)−Zn(5)−O(8)	113.7(2)
O(12)−Zn(6)−N(11)	108.4(3)	O(12)−Zn(6)−N(12)	103.1(3)
O(12)−Zn(6)−O(7)	105.4(2)	O(12)−Zn(6)−O(8)	99.7(2)
O(11)−Zn(7)−N(13)	109.0(3)	O(11)−Zn(7)−N(14)	99.2(2)
O(11)−Zn(7)−O(9)	112.7(2)	O(11)−Zn(7)−O(10)	99.5(2)
O(12)−Zn(8)−N(15)	114.1(3)	O(12)−Zn(8)−N(16)	101.2(2)
O(12)−Zn(8)−O(9)	100.6(2)	O(12)−Zn(8)−O(10)	106.8(2)
2b			
Zn(1)−O(6)	1.942(5)	Zn(2)−O(5)	1.956(5)
Zn(3)−O(5)	1.950(5)	Zn(4)−O(6)	1.937(5)
O(6)−Zn(1)−N(1)	108.8(2)	O(6)−Zn(1)−O(2)	105.0(2)
O(6)−Zn(1)−N(2)	103.1(2)	O(6)−Zn(1)−O(1)	96.8(2)
O(5)−Zn(2)−N(3)	105.5(3)	O(5)−Zn(2)−O(1)	112.8(2)
O(5)−Zn(2)−N(4)	106.7(2)	O(5)−Zn(2)−O(2)	98.8(2)
O(5)−Zn(3)−N(7)	107.4(2)	O(5)−Zn(3)−N(8)	105.6(2)
O(5)−Zn(3)−O(3)	105.9(2)	O(5)−Zn(3)−O(4)	101.8(2)
O(6)−Zn(4)−N(5)	102.6(2)	O(6)−Zn(4)−N(6)	111.6(2)
O(6)−Zn(4)−O(3)	99.4(2)	O(6)−Zn(4)−O(4)	106.2(2)

atoms in a *trans* position of the macrocycle to decrease steric repulsion. It should be noted that there is a π−π interaction between parts of two rings in **2**; this is believed to strengthen two hydroxyl groups connecting the metal atoms in the same direction of the macrocycle.



2a

2b

Figure 2. Views of molecular packing in crystals of **2a** (top) and **2b** (bottom); solvent molecules and perchlorate anions have been omitted

Structural Description of $\{[Zn_2L^a(H_2O)_2(C_{10}H_9N)_2](ClO_4)_2\}$ (3a)

A single crystal X-ray diffraction study confirmed that the coordination geometry about the two metal atoms in compound **3a** is the same as that in **1**, with two water molecules occupying two apical positions at the opposite side of the macrocyclic plane like **3b** (Figure 4), although the position of the substituted methyl group is different in **3a** and **3b**. There are two crystallographically independent half molecules $[Zn_2L^a(H_2O)_2(C_{10}H_9N)]^{2+}$ in the asymmetric unit, each half molecule being related to another half by a centre of symmetry, giving a total of two molecules in the unit cell. The main bond lengths and angles of complex **3a** are given in Table 3. The zinc(II) atom is situated slightly above the N_2O_2 plane and each metal may be considered as distorted square pyramidal. It has also been clearly observed that two nitrogen atoms from two 2-methylquinoline molecules are linked to two coordinating water molecules above and below the macrocyclic framework, through hydrogen bonds. The resulting two N···H−O hydrogen bonds are the same with N···H, H−O, and N···O lengths of 1.865 Å, 0.809 Å, and 2.663 Å, respectively, and an N···H−O angle of 169.13°. It is very interesting to note that two hydrogen-bonded quinoline rings are found in an almost parallel position to the phenyl ring in the macrocyclic plane (with a dihedral angle of 6.3°). Moreover, they lie in a face-to-face fashion with the adjacent macrocyclic frameworks on their other side. The two quinoline rings situated between two macrocycles are strictly coplanar to each other (with a di-

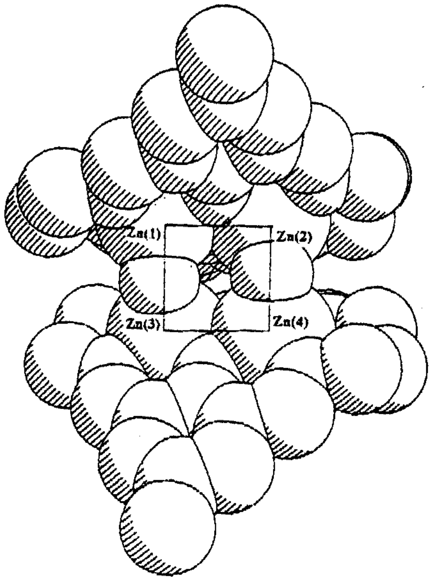


Figure 3. Space-filling view of the Zn_4 array in **2a**; hydrogen atoms are omitted for clarity

Table 2. Geometric dimensions [Å, deg] of the Zn_4 array in **2a** and **2b**

2a			
Zn(1)−Zn(2)	3.133	Zn(5)−Zn(6)	3.128
Zn(3)−Zn(4)	3.126	Zn(7)−Zn(8)	3.100
Zn(1)−Zn(3)	3.593	Zn(5)−Zn(7)	3.514
Zn(2)−Zn(4)	3.628	Zn(6)−Zn(8)	3.561
Zn(2)−Zn(1)−Zn(3)	84.7	Zn(6)−Zn(5)−Zn(7)	93.1
Zn(1)−Zn(2)−Zn(4)	92.6	Zn(5)−Zn(6)−Zn(8)	83.9
Zn(1)−Zn(3)−Zn(4)	93.4	Zn(5)−Zn(7)−Zn(8)	85.1
Zn(2)−Zn(4)−Zn(3)	84.3	Zn(6)−Zn(8)−Zn(7)	92.7
2b			
Zn(1)−Zn(2)	3.145		
Zn(3)−Zn(4)	3.162		
Zn(1)−Zn(3)	3.665		
Zn(2)−Zn(4)	3.586		
Zn(2)−Zn(1)−Zn(3)	84.5		
Zn(1)−Zn(2)−Zn(4)	85.6		
Zn(1)−Zn(3)−Zn(4)	92.4		
Zn(2)−Zn(4)−Zn(3)	94.2		

hedral angle of 0.0°), forming an ordered arrangement where one macrocycle and two 2-methylquinolines are alternately arrayed (Figure 5). The separations between the macrocyclic and quinoline rings are all about 3.6 Å. It is proposed that π−π interactions are present between quinoline and phenyl species in the macrocyclic skeleton, where the electron-rich quinoline moiety (uncoordinated) acts as a donor and the electron-poor phenyl species (owing to the coordination of the macrocyclic ligand) as acceptors. It is suggested that both the π−π interactions and the H-bonding interactions dominate such a stacking structure.

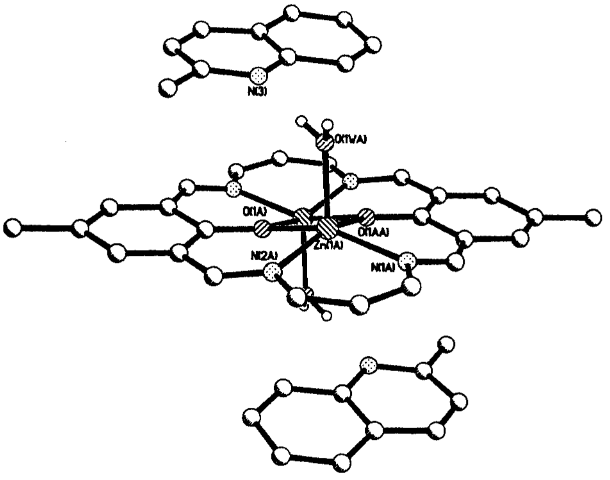


Figure 4. Ball-and-stick representation of the structure of one of the centrosymmetric complex cations from **3a**; only one of the two dinuclear clusters is shown as they are very similar

Our previous studies show that the coordinating water molecules on two sides of the macrocyclic framework can be replaced by a ligand if linear inorganic ligands or organic alkyl ligands are allowed to react with **1**.[12] However, based on the results of **2**, monofunctional aromatic ligands such as pyridine cannot be bonded to the metal atom of **1** at the vertical direction only by one-end coordination bonding, nor can the bidentate chelating ligand 2,2′-bipyridine. This may arise from the spatial repulsion between the macrocycle and the aromatic ring. Such a repulsion could be overcome, however, to permit coordination if extra forces are introduced such as hydrogen bonding or π−π interactions to support the system.[5,6] While in compound **3a** 2-methylquinoline cannot be coordinated directly to the zinc(II) atoms because of its further steric repulsion, it instead adopts a parallel way of interacting with its neighboring macrocyclic plane via π−π forces while, at the same time, forming a hydrogen bond with one macrocyclic unit. The electron transfer from the conjugated system of the macrocycle to the central zinc(II) atom upon coordination assists in forming this kind of arrangement. To the best of our knowledge, **3a** and **3b** are unprecedented examples where a macrocyclic dinuclear metal component serves as an acceptor to produce donor-acceptor compounds sustained by hydrogen bonds.

In recent years, progress in the study of the aggregation of molecular building blocks by self-assembly has risen dramatically, and several studies indicate that the results of self-assembly and the topology of metal-ligand frameworks are mainly upon the application of specific center metal atoms and well-built organic ligands.[13] In our series of experiments, the effect of the coordination geometry of the zinc atom in **1** has been investigated. Based on these and previous results, it is suggested that the coordination behavior of

Table 3. Main bond lengths [Å] and angles [deg] in **3a**

Zn(1A)−O(1WA)	2.007	H(2WA)···N(3)	1.865
O(1WA)−Zn(1A)−N(1A)	105.08(16)	O(1WA)−Zn(1A)−O(1A)	102.65(14)
O(1WA)−Zn(1A)−N(2A)	101.05(16)	O(1WA)−Zn(1A)−O(1AA)	99.27(13)
O(1WA)−H(2WA)···N(3)	169.11(10)		

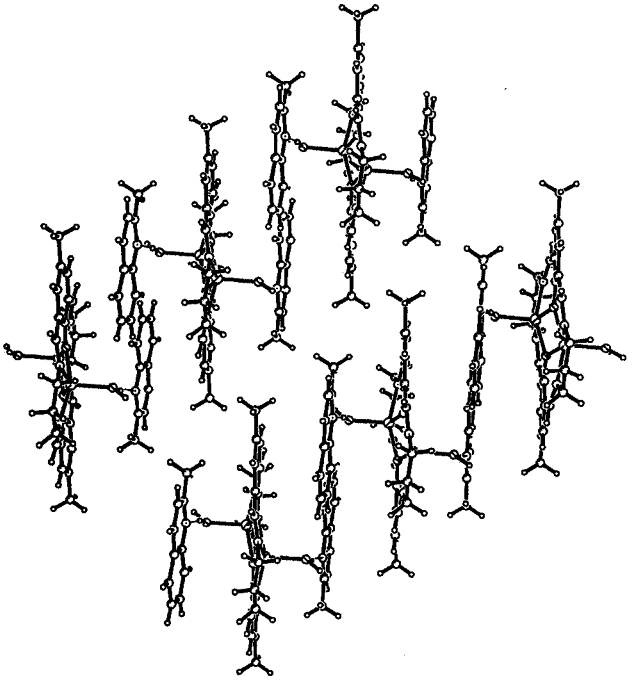


Figure 5. Packing view of **3a** along the *c*-axis; perchlorate anions have been omitted

the metal atom plays an important role in the assembly pattern of **1** with aromatic building blocks.

Experimental Section

Materials and General Methods: The perchlorate salts of **1a** and **1b** were prepared in the same manner as reported previously.[12] All other solvents and chemicals were of analytical grade and used without further purification.

Elemental analyses were measured with a Perkin−Elmer 1400C analyser. Infrared spectra (4000−400 cm^{-1}) were recorded on a Nicolet FT-IR 170X spectrophotometer. ^1H NMR spectra were obtained on a Bruker 500 MHz NMR spectrometer. Electrospray ionization (ES) mass spectra were performed in CH_3CN/CH_3OH on a Finnigan MAT SSQ 710 mass spectrometer in a scan range 300−1200 amu.

Caution! *Although no problem was encountered in all our experiments, transition metal perchlorates are potentially explosive and should be handled in small quantities.*

Preparation

2a: Pyridine (0.08 g, 1 mmol) was added to a solution of **1a** perchlorate (0.37 g, 0.5 mmol) in ethanol (30 cm^3). The solution was refluxed for 1 h, and then cooled to room temperature. Yellow crystal products were obtained, which were washed with a small amount of ethanol and dried in a vacuum. Yield 0.29 g (87%); Elemental analyses: $[C_{48}H_{52}N_8O_4Zn_4(OH)_2](ClO_4)_2(C_2H_5OH)(H_2O)_2$ (M = 1381.53): calcd. C 44.04, H 4.58, N 8.22; found C 44.16, H 4.81, N 8.21%. IR (KBr): $\tilde{\nu}$ [cm^{-1}]: 3512 s (O−H), 1641 s (C=N), 1088 vs and 623 s (ClO_4^-). ES-MS: m/z = 632 $[(Zn_2C_{24}H_{26}N_4O_2)(ClO_4)]^+$ (100%). ^1H NMR (500 MHz, D_2O, 25 °C, TMS) [ppm]: δ = 2.15 (m, 8 H, CH_2), 2.30 (s, 12 H, CH_3), 4.05 (t, 16 H, CH_2), 7.44 (s, 8 H, phenyl), 8.36 (s, 8 H, HC=N).

2b: This preparation is similar to that of **2a**, except that **1b** perchlorate (0.37 g, 0.5 mmol) and 2,2′-bipyridine (0.16 g, 1 mmol) were used. Yield 0.29 g (84%); Elemental analyses: $[C_{44}H_{40}N_8O_4Cl_4Zn_4(OH)_2](ClO_4)_2(C_2H_5OH)(H_2O)_2$ (M = 1463.20): calcd. C 37.76, H 3.58, N 7.66; found C 37.51, H 3.36, N 7.43%. IR (KBr): $\tilde{\nu}$ [cm^{-1}]: 3533 s (O−H), 1643 s (C=N), 1083 vs and 623 s (ClO_4^-). ES-MS: m/z = 337 $\{[(Zn_2C_{22}H_{20}Cl_2N_4O_2)(HClO_4)]^{2+}\}/2$ (100%). ^1H NMR (500 MHz, D_2O, 25 °C, TMS) [ppm]: δ = 2.16 (m, 8 H, CH_2), 4.05 (t, 16 H, CH_2), 7.64 (s, 8 H, phenyl), 8.36 (s, 8 H, HC=N).

3a: 2-Methylquinoline (0.14 g, 1 mmol) was added to an ethanol solution (30 cm^3) of **1a** perchlorate (0.37 g, 0.5 mmol). The solution was refluxed for 1 h and then cooled to room temperature. The yellow precipitate was filtered, washed with a small amount of ethanol, and dried in vacuum. Yield 0.45 g (88%); Elemental analyses: $[C_{24}H_{26}N_4O_2Zn_2(H_2O)_2(C_{10}H_9N)_2](ClO_4)_2$ (M = 1054.56): calcd. C 50.11, H 4.59, N 7.97; found C 50.28, H 4.64, N 7.86%. IR (KBr): $\tilde{\nu}$ [cm^{-1}]: 3377 s (O−H), 1640 s (C=N), 1087 vs and 625 s (ClO_4^-). ES-MS: m/z = 591 $[ZnNaHLClO_4]^+$ (100%). ^1H NMR (500 MHz, D_2O, 25 °C, TMS) [ppm]: δ = 2.26 (m, 4 H, CH_2), 2.43(s, 6 H, CH_3), 2.89 (s, 6 H, CH_3 of quinoline ring), 4.14 (t, 8 H, CH_2), 7.57 (s, 4 H, phenyl), 7.68−8.12 (m, 8 H, quinoline ring), 8.48 (s, 4 H, HC=N), 8.55 (m, 4 H, quinoline ring).

3b: The preparation is analogous to **3a** except that that 8-methylquinoline (0.14 g, 1 mmol) was employed. Yield: 0.46 g (90%). Elemental analyses: $[C_{24}H_{26}N_4O_2Zn_2(H_2O)_2(C_{10}H_9N)_2](ClO_4)_2$ (M = 1054.56): calcd. C 50.11, H 4.59, N 7.97; found: C 50.44, H 4.73, N 8.21. IR (KBr): $\tilde{\nu}$ [cm^{-1}]: 3375 s (O−H), 1641 (C=N), 1087 vs and 624 s (ClO_4^-). Es-ms: m/z = 591 $[ZnNaHLClO_4]^+$ (100). ^1H NMR (500 MHz, D_2O, 25 °C, TMS) [ppm]: δ = 2.25 (m, 4 H, CH_2), 2.41 (s, 6 H, CH_3), 2.84 (s, 6 H, CH_3 of quinoline ring), 4.16 (t, 8 H, CH_2), 7.55 (s, 4 H, phenyl), 7.65−8.10 (m, 8 H, quinoline ring), 8.46 (s, 4 H, HC=N), 8.55 (m, 4 H, quinoline ring).

Crystallography

Single crystals of all compounds suitable for X-ray diffraction measurements were grown from their ethanol/methanol solutions. The molecular structure of **3b** has been reported elsewhere where only 8-methylquinoline was used to assemble **1a**.[14] Because crystals of **2a**, **2b**, and **3a** are very unstable in the absence of their mother liquors, their single-crystal samples were covered in glue before measurements. Reflection data for three crystals were measured by a Bruker SMART 1K CCD diffractometer system at 293(2) K by using graphite monochromated Mo-K_α radiation (λ =

Table 4. Summary of crystal data of **2a**, **2b**, and **3a**

Compound	**2a**	**2b**	**3a**
Chem. formula	$C_{99}H_{118}Cl_4N_{16}O_{32}Zn_8$	$C_{45}H_{48}Cl_6N_8O_{17}Zn_4$	$C_{44}H_{48}Cl_2N_6O_{12}Zn_2$
M	2708.85	1447.09	1054.52
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	*P 21/c*	$P\bar{1}$	$P\bar{1}$
a [Å]	26.5214(4)	13.47870(10)	8.8057(1)
b [Å]	23.4111(3)	15.6702(2)	12.4797(3)
c [Å]	17.8921(2) A	17.3503(3)	21.6900(5)
α [deg]	90.00	63.6995(7)	91.704(1)
β [deg]	103.6923(7)	78.0460(8)	95.942(1)
γ [deg]	90.00	71.3850(9)	102.874(1)
V [Å^3]	10793.4(2)	3104.08(7)	2307.74(8)
Z	4	2	2
D_{calcd} [g·cm^{-3}]	1.667	1.548	1.520
μ [mm^{-1}]	1.933	1.853	1.224
F(000)	5552	1464	1092
Crystal size [mm]	0.34 × 0.18 × 0.14	0.48 × 0.38 × 0.32	0.40 × 0.20 × 0.14
2θ range for data collection	5.46 to 57.98	5.38 to 56.64	1.90 to 56.60
no. of reflns meads, unique	76717, 27472	22352, 14835	16497, 10859
no. of reflns with [$I > 2\sigma(I)$]	9912	6215	4592
max., min. transmission	0.7736, 0.5594	0.5885, 0.4699	0.8473, 0.6403
*R*1, *wR*2 [$I > 2\sigma(I)$]	0.0921, 0.1690	0.0765, 0.2074	0.0638, 0.1502
*R*1, *wR*2 [all data]	0.2581, 0.2313	0.1671, 0.2458	0.1547, 0.1788
Goodness of fit on F^2	0.954	0.902	0.855
|*ρ*, max, min [e·Å^{-3}]	0.989, −0.684	0.823, −0.754	0.859, −0.826

0.71073 Å). The data were collected by using SMART and reduced with the program SAINT.[15] Empirical absorption correction was done by using the SADABS program.[16] All structures were solved by direct methods and refined by least-squares method on F^2_{obs} with the SHELXTL-PC software package.[17] All non-H atoms, except the oxygen atoms from two perchlorate ions and solvent molecules in **2b**, were refined anisotropically. The hydrogen atom positions were fixed geometrically and allowed to ride on the attached atoms. One middle carbon atom of the 1,3-diaminopropane in one macrocyclic unit in **2b** was found to be disordered over two sites, with an occupancy of 0.48(3) and 0.52(3) for C-13. Crystal data and structural refinement for three compounds are listed in Table 4.

CCDC-140749 (**2a**), -140750 (**2b**), and -157365 (**3a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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