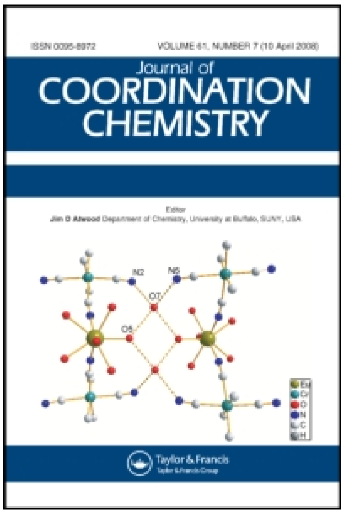

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Synthesis and crystal structures of 3D supramolecular compounds: [<i>M</i>(4,4'-bipy)$_2$(H$_2$O)$_4$] · (4,4'-bipy)$_2$ · (3,5-daba)$_2$ · 8H$_2$O (<i>M</i>=Zn, Mn)

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Synthesis and crystal structures of 3D supramolecular compounds: [M(4,4′-bipy)$_2$(H$_2$O)$_4$]·(4,4′-bipy)$_2$·(3,5-daba)$_2$·8H$_2$O (M = Zn, Mn)

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Two new supramolecular compounds [M(4,4′-bipy)$_2$ (H$_2$O)$_4$]·(4,4′-bipy)$_2$·(3,5-daba)$_2$·8H$_2$O (M=Zn(**1**) or Mn(**2**), 4,4′-bipy = 4,4′-bipyridine, 3,5-daba = 3,5-diaminobenzoic acid anion) were synthesized and characterized by elemental analysis and X-ray crystal diffraction. In [M(4,4′-bipy)$_2$(H$_2$O)$_4$]$^{2+}$, the M(II) is coordinated by two nitrogen atoms from two 4,4′-bipy molecules and four oxygen atoms from four waters to form an octahedral configuration. There exist uncoordinated 4,4′-bipy molecules, 3,5-diaminobenzolate counterions and water guests in the compounds. The 3D structures of the title supramolecular compounds are constructed by rich hydrogen bonds among [M(4,4′-bipy)$_2$(H$_2$O)$_4$]$^{2+}$, uncoordinated 4,4′-bipy molecules, water molecules and 3,5-daba, containing a diverting hexa-member water ring.

Keywords: 4,4′-bipy; Water ring; Hydrogen bonds; Supramolecular compounds

1. Introduction

Supramolecular architectures based on metal-ligand and noncovalent interactions have provided beautiful and diversified structures and potential applications. Hydrogen bonding plays a very important role in the construction of supramolecular architectures [1]. The strength of multiple hydrogen bonds is roughly comparable with that of a metal-ligand coordination bond; as these possess the capability of molecular recognition and directionality, they have been exploited in supramolecular chemistry and crystal engineering [2]. 4,4′-bipy is an excellent rigid bridging ligand, capable of forming weak intermolecular interaction such as hydrogen bonding and π–π stacking. It is essential to study syntheses and crystal structures of complexes formed by 4,4′-bipy systematically, and to inquire into the factors that influence the

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formation and structures of such a complex. Such a studies may lead to design and synthesis of functional materials, and also provide theoretical foundations for supramolecular chemistry and crystal engineering [3]. Carboxylate ligands can bind to metal ions to form coordination polymers and are also capable of functioning as hydrogen bond donors or acceptors [4]. Water, important for hydrogen bond networks, especially morphologies of water clusters in diverse chemical environments provides quantitative characterization of hydrogen-bonded networks in liquid water or ice. Water clusters including tetramers [5], hexamers [6], octamers [7] and decamers [8] have been structurally characterized; hydrogen-bonding interaction and their fluctuations are the key to formation of water clusters [9, 10].

Herein 4,4′-bipy and 3,5-diaminobenzoic acid ligands gave $[M(4,4'\text{-bipy})_2(H_2O)_4]\cdot(4,4'\text{-bipy})_2\cdot(3,5\text{-daba})_2\cdot 8H_2O$ (M=Zn(**1**), Mn(**2**)), as new building blocks for hydrogen-bonded self-assembling networks, with two new 3D supramolecular structures via abundant self-complementary and complementary hydrogen-bonding among $[M(4,4'\text{-bipy})_2(H_2O)_4]^{2+}$, uncoordinated 4,4′-bipy molecules, water molecules and 3,5-daba.

2. Experimental

2.1. *Synthesis of 1 and 2*

Preparation of **1**: A solution of 4,4′-bipyridine (0.156 g, 1 mmol) and 3,5-diaminobenzoic acid (0.152 g, 1 mmol) in water (8 mL) was slowly added to a solution of $ZnCl_2\cdot 4H_2O$ (0.136 g, 1 mmol) in distilled water (8 mL). The mixture was stirred for 10 min at 298 K and placed in a 23 mL Teflon-lined autoclave and heated at 120°C for 120 h. The autoclave was cooled over a period of 8 h at $10^\circ C\,h^{-1}$, and **1** as colorless block crystals were collected by filtration, and dried at ambient temperature. Yield: 0.14 g (51%, based on Zn). The synthesis of **2** is similar to **1** with $MnCl_2\cdot 4H_2O$ instead of $ZnCl_2\cdot 4H_2O$. Anal. Calcd for $C_{54}H_{70}ZnN_6O_{16}$ (**1**): C, 57.67; H, 6.27; N, 7.47. Found (%): C, 57.25; H, 6.48; N, 7.41. $C_{54}H_{70}MnN_6O_{16}$ (**2**): C, 58.22; H, 6.33; N, 7.54. Found (%): C, 58.01; H, 6.48; N, 7.43.

2.2. *Single-crystal structure determination*

Intensity data for **1** and **2** were collected at 298 K on a Bruker SMART CCD area-detector diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the ω–θ scan mode both in the range $2.1 \leq \theta \leq 25^\circ$. Raw frame data were integrated with the SAINT [11] program. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on F^2 using SHELXS-97 [12]. An empirical absorption correction was applied with SADABS [13]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined by a riding mode, with a common thermal parameter. All calculations and graphics were performed with SHELXTL [12]. The crystallographic data and experimental details for the structure analysis are summarized in table 1.

Table 1. Crystallographic data and intensity collection details for **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{54}H_{70}ZnN_6O_{16}$	$C_{54}H_{70}MnN_6O_{16}$
Formula weight	1208.61	1198.16
Crystal system	Monoclinic	Monoclinic
Space group	$P2/c$ (No. 13)	$P2/c$ (No. 13)
Color/shape	Colorless/block	Colorless/block
a (Å)	9.392(2)	9.397(2)
b (Å)	7.769(2)	7.778(1)
c (Å)	39.289(3)	39.529(3)
β (°)	90.108(2)	90.141(2)
V (Å^3)	2866.7(9)	2888.9(7)
Z	2	2
T (K)	298	298
$F(000)$	1272	1262
D_c g cm^{-3}	1.400	1.377
Goodness-of-fit on F^2	1.05	1.02
Theta range (°)	2.1, 25.0	2.1, 25.0
F_{max}/F_{min} (e Å^{-3})	0.34, −0.70	0.28, −0.39
μ (mm^{-1})	0.51	0.31
Total reflections	14369	14356
Unique reflections	5056	5106
R_{int}	0.036	0.052
R_1 [$I \geq 2(I)$]	0.0497	0.0556
wR_2 (all data)	0.1197	0.1407

3. Results and discussion

The selected bond lengths and angles are listed in table 2. The molecular structure of **1** with atomic numbering scheme is shown in figure 1. Compound **1** consists of sheet-like arrays of monomeric $[Zn(4,4'\text{-bipy})_2(H_2O)_4]^{2+}$ cations connected by uncoordinated bipy molecules, water molecules and 3,5-diaminobenzolate counterions. The ZnN_2O_4 unit adopts a slightly distorted octahedral geometry, being coordinated axially by two *trans*-related 4,4′-bipyridine ligands with the equatorial sites occupied by four aqua ligands. The pyridyl rings of the bipy ligands are not coplanar but twisted along the central C–C bonds at angles of 26.1° (**1**, plan equation: $-1.286x + 7.530y - 8.006z = -5.1634$) and 26° (**2**, plan equation: $-2.716x - 6.971y - 13.124z = -6.7468$) with respect to one another. The monomeric $[Zn(4,4'\text{-bipy})_2(H_2O)_4]^{2+}$ cations form stacks along the *b*-axis (figure 2). The uncoordinated pyridyl rings of the bipy ligands and water molecules interdigitate with those in adjacent stacks giving rise to pseudo two-dimensional sheets. The sheets of monomers are well separated by uncoordinated bipy molecules, water molecules and 3,5-diaminobenzolate counterions. The uncoordinated bipy's crosslink the sheets through an extensive array of $N \cdots H\text{–}O$ hydrogen bonds (2.86–2.87 Å) between the uncoordinated pyridyl nitrogen atoms and nearby aqua ligands, giving a hydrogen-bonded network.

There exist abundant hydrogen bonds between water guests. Three of the four crystallographically independent water molecules (O5, O6 and O8) are located at the 2-fold rotation axes and hydrogen-bond to each other ($O5\text{–}H \cdots O8 = 2.767(3)$ Å, $O6\text{–}H \cdots O8 = 2.800(3)$ Å, $O5A\text{–}H \cdots O5 = 2.824(3)$ Å, $O6A\text{–}H \cdots O6 = 2.765(3)$ Å, tables 3 and 4). These water molecules form an unusual quasi-planar cyclic hexamer (figure 3) [14]. Adjacent hexamers are assembled in a side-to-side fashion along the

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1		**2**	
Zn1–O3	2.130(2)	Mn1–O3	2.196(3)
Zn1–O4	2.120(2)	Mn1–O4	2.184(3)
Zn1–N3	2.132(2)	Mn1–N3	2.253(3)
O3–Zn1–O4	92.56(8)	O3–Mn1–O4	92.7(1)
O3–Zn1–N3	89.35(9)	O3–Mn1–N3	88.1(1)
O3–Zn1–O3a	86.75(8)	O3–Mn1–O3a	85.8(1)
O3–Zn1–O4a	178.44(8)	O3–Mn1–O4a	178.4(1)
O3–Zn1–N3a	89.58(9)	O3–Mn1–N3a	90.5(1)
O4–Zn1–N3	89.02(9)	O4–Mn1–N3	88.7(1)
O3a–Zn1–O4	178.44(8)	O3a–Mn1–O4	178.4(1)
O4–Zn1–O4a	88.16(8)	O4–Mn1–O4a	88.7(1)
O4–Zn1–N3a	92.05(9)	O4–Mn1–N3a	92.6(1)
O3a–Zn1–N3	89.58(9)	O3a–Mn1–N3	90.5(1)
O4a–Zn1–N3	92.05(9)	O4a–Mn1–N3	92.6(1)
N3–Zn1–N3a	178.52(9)	N3–Mn1–N3a	178.1(1)
O3a–Zn1–O4a	92.56(8)	O3a–Mn1–O4a	92.7(1)
O3a–Zn1–N3a	89.35(9)	O3a–Mn1–N3a	88.1(1)
O4a–Zn1–N3a	89.02(9)	O4a–Mn1–N3a	88.7(1)

Symmetry code: **1**: $1-x$, y, $3/2-z$; **2**: $2-x$, y, $3/2-z$.

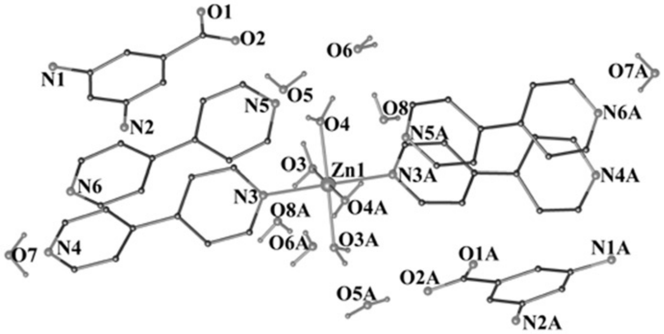

Figure 1. The Zn(II) coordination environment in the monomeric subunit in **1**, some hydrogen atoms have been omitted for clarity.

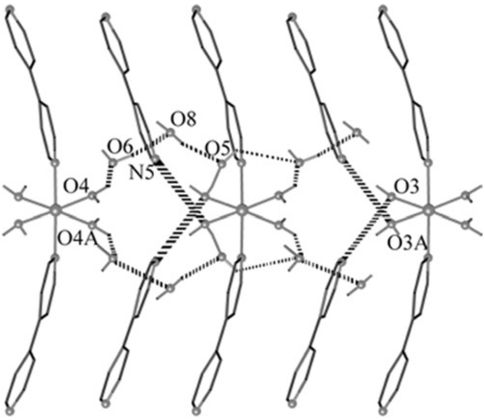

Figure 2. 1D chain along the *b*-axis for **1**.

Table 3. Hydrogen bond lengths (Å) and angles (°) for **1**.

D–H···A	Symmetry code	D–H	H–A	D···A	∠DHA
N1–H1A···N4	$x, 1+y, z$	0.8610	2.3832	3.132(4)	145.66
N1–H1B···O7		0.8598	2.1588	3.015(4)	174.08
N2–H2A···O7	$x, 1+y, z$	0.8608	2.3400	3.113(4)	149.54
N2–H2B···O1	$x, 1+y, z$	0.8590	2.3635	3.132(4)	149.16
O3–H28···N5	$x, -1+y, z$	0.8502	2.0124	2.862(4)	177.97
O3–H29···O5	$1-x, 1-y, 1-z$	0.8503	1.8987	2.743(3)	171.91
O4–H30···N5		0.8493	2.4055	3.254(4)	177.03
O4–H31···O6		0.8498	1.7959	2.645(3)	177.32
O5–H32···O2		0.8510	1.8931	2.740(3)	173.45
O5–H33···O5		0.8510	1.9964	2.824(3)	163.82
O6–H34···O2		0.8511	1.7947	2.641(4)	172.94
O6–H35···O8		0.8502	1.9910	2.800(3)	158.58
O7–H36···N1	$-x, 1-y, 1-z$	0.8498	2.1821	3.025(4)	171.13
O7–H37···N6		0.8498	2.0471	2.869(4)	162.57
O8–H38···O5		0.8499	1.9752	2.767(3)	154.55
O8–H39···O1		0.8494	1.8881	2.713(3)	163.45

Table 4. Hydrogen bond lengths (Å) and angles (°) for **2**.

D–H···A	Symmetry code	D–H	H–A	D···A	∠DHA
N1–H1A···N4	$1-x, 1-y, 1-z$	0.8610	2.3679	3.119(4)	146.03
N1–H1B···O8	$1-x, -y, 1-z$	0.8596	2.1735	3.029(4)	173.53
N2–H2A···O8	$1-x, 1-y, 1-z$	0.8595	2.3587	3.133(4)	150.14
N2–H2B···O2	$x, 1+y, z$	0.8594	2.3697	3.140(4)	149.48
O3–H3A···N5		0.8492	2.0252	2.870(4)	172.77
O3–H3B···O6	$1+x, y, z$	0.8512	1.9014	2.743(4)	169.60
O4–H4B···N5	$x, -1+y, z$	0.8490	2.4215	3.220(5)	156.94
O4–H4C···O7 2	$x, y, 3/2-z$	0.8506	1.8948	2.633(4)	144.29
O5–H5A···O6		0.8497	1.9353	2.764(4)	164.56
O5–H5B···O2	$x, 1+y, z$	0.8495	1.8843	2.712(4)	164.17
O6–H6A···O1		0.8496	1.8954	2.743(4)	175.20
O6–H6B···O6	$1-x, y, 3/2-z$	0.8481	1.9869	2.833(4)	175.12
O7–H7A···O1		0.8487	1.8268	2.652(4)	163.74
O7–H7B···O5	$x, -1+y, z$	0.8504	1.9617	2.791(4)	164.64
O8–H8A···N1		0.8502	2.1934	3.040(4)	173.59
O8–H8B···N6	$x, -1+y, z$	0.8484	2.0345	2.879(4)	173.19

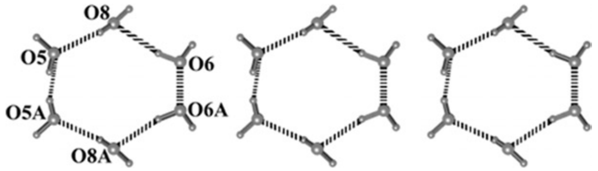

Figure 3. Hydrogen-bonding environments of the guest water molecules along the *a*-axis.

a-axis to give an extended water ring occupying the groove of the surface. The water rings are separated from each other (>9 Å) and connected with coordinated aqua ligands through hydrogen-bonded (O4–H$\cdots$O6 = 2.645(3) Å). Stacks of water guests define hydrophilic chains along the *a*-axis that clathrate 3,5-diaminobenzolate counterions. The 4,4′-bipy ligands in two compounds locate on both sides of the chains in a *cis*-arrangement, and these layers run along the *c*-axis, stacking in

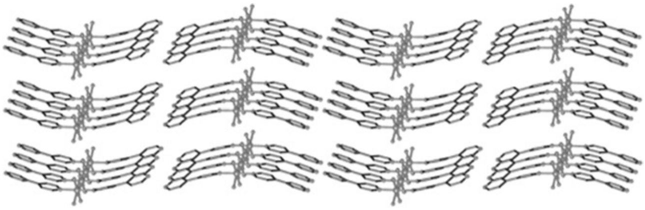

Figure 4. 3D supermolecular framework for **1**.

the sequence ABAB with the plane of 4,4′-bipy ligands of adjacent layers arranged in face-face stacking modes (figure 4). Plane-plane distances between coordinated 4,4′-bipy aromatic groups of adjacent layers are Ca 9.361 Å for **1** and 9.42(1) Å for **2**. However, the plane-plane distances between coordinated and uncoordinated 4,4′-bipy aromatic groups of the adjacent layers are 3.72(1) and 3.66(1) Å in **1** and **2**, respectively. Thus, the weak π–π stacking and strong hydrogen-bonded interactions extend the 2D layers into a 3D supermolecular framework.

In summary, we have hydrothermally synthesized and obtained crystal structures of two new 3D supramolecular complexes with 4,4′-bipy, in which a water hexamer is observed. The structures are 3D supermolecular frameworks via weak π–π stacking and strong hydrogen bonding. An unusual quasi-planar water hexamer was embedded in the 3D structure via supramolecular interaction. This study demonstrates that the nature of the ligand and the geometric needs of the metal atoms play important roles in the crystal packing of coordination polymers but that hydrogen bonds affect the formation of supramolecular architectures.

Supplementary data

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 664525 and 664524 for **1** and **2**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: 44 1223-336-033; Email: deposit@ccdc.cam.ac.uk].

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