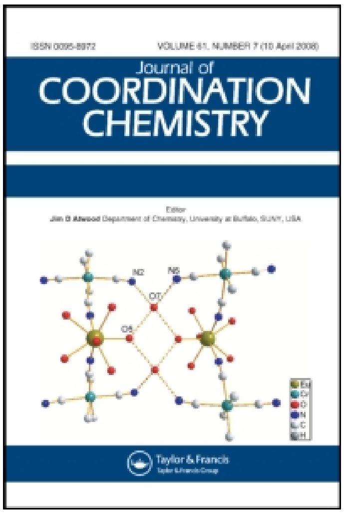

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INCLUSION AND INTERCALATION OF 4,4′-BIPYRIDINE IN A ZINC(II) AQUA PERCHLORATO COMPLEX $[Zn(4,4'\text{-bpy})(H_2O)_3(ClO_4)](ClO_4)\cdot(4,4'\text{-bpy})_{1.5}\cdot H_2O$

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A novel 4,4′-bipyridine's zinc(II) aqua perchlorato complex $[Zn(4,4'\text{-bpy})(H_2O)_3(ClO_4)](ClO_4)\cdot(4,4'\text{-bpy})_{1.5}\cdot H_2O$ (where 4,4′-bpy = 4,4′-bipyridine) has been synthesized by self-assembly. The crystal structure consists of zinc ion chains $[Zn(4,4'\text{-bpy})(H_2O)_3(ClO_4)]$ bridged by coordinated 4,4′-bpy molecules. Two chains related by a centre of inversion are interconnected by hydrogen bonds between coordinated water molecules and coordinated perchlorate anions to form a two-dimensional "ladder" with cavities enclosing uncoordinated 4,4′-bpy molecules whereas other 4,4′-bpy molecules are intercalated in between the "ladder" layers. All these 4,4′-bpy molecules are hydrogen bonded to coordinated water molecules as another kind of bridge to extend the structure into a three-dimensional network in the solid.

Keywords: Zinc(II); 4,4′-bipyridine; crystal structure; self-assembly; coordination polymers; inclusion

INTRODUCTION

Coordination polymers containing 4,4′-bipyridine(4,4′-bpy) as bridging ligands have aroused increasing interest due to both theoretical aspects related to the topologies of novel networks and their potential applications.[1–4] The inclusion ability of the cavity structures could be utilized in separation

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[*] Corresponding author.

of guest molecules from their isomeric mixtures, and also in the heterogeneous catalysis field.[5] We now report a novel zinc(II) complex $[Zn(4,4'\text{-bpy})(H_2O)_3(ClO_4)](ClO_4)\cdot(4,4'\text{-bpy})_{1.5}\cdot(H_2O)$ (1), where 4,4′-bpy is inclosed and intercalated in its zinc(II) aqua perchlorato complex.

EXPERIMENTAL

Synthesis of $[Zn(4,4'\text{-bpy})(H_2O)_3(ClO_4)](ClO_4)\cdot(4,4'\text{-bpy})_{1.5}\cdot(H_2O)$

Reflux of an methanol-aqueous solution (v/v 1 : 1, 40 cm^3) of 4,4′-bipyridine (3 mmol) and $Zn(ClO_4)_2\cdot 6H_2O$ (1 mmol) for 1 h gave a transparent solution. Colourless single crystals suitable for X-ray diffraction study were easily obtained by slow evaporation at room temperature over a few days (yield 85%). *Anal.*, Calc. For $C_{25}H_{28}Cl_2N_5O_{12}Zn$ (%): C, 41.3; H, 3.9; N, 9.6. Found: C, 41.2; H, 4.0; N, 9.5.

Elemental analyses were performed on a Perkin Elmer 240 instrument. IR spectra were recorded in KBr pellets in the range 4000–400 cm^{-1} using a Nicolet 170SX FTIR spectrophotometer. Thermogravimetric and differential thermal analyses were performed on a Perkin Elmer thermal analyzer under flowing N_2 with a heating rate of 10°C/min.

Crystallographic Analysis

A colourless needle with dimensions 0.43 × 0.36 × 0.36 mm was employed for structural analysis on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å). Unit cell parameters were determined by least-squares methods based on the setting angles ($5 < \theta < 10°$) of 15 reflections. Intensity data were measured using the ω–2θ scan technique with variable scan speed. Of the 5419 independent reflections in the range $1.29 < \theta < 25.05°$, 4274 with $I > 2\sigma(I)$ were used in structure solution and refinement. The raw data were corrected for Lorentz polarization effects and absorption (Psi-scan technique).[6]

The structure was solved by the Patterson method using SHELXS 86,[7] and refined using SHELXL 93.[8] Coordinates and the anisotropic thermal parameters for non-hydrogen atoms were refined by full-matrix least-squares. All H atoms were generated geometrically, allowed to ride on the atoms to which they are attached and refined isotropically. The refinement was based on wF_o^2, where $w = 1/[\sigma^2(F_o)^2 + (0.0773P)^2 + 1.2700P]$ and $P = (F_o^2 + 2F_c^2)/3$. A summary of crystallographic data and additional data collection parameters is given in Table I. Final atomic coordinates are listed in Table II.

TABLE I Crystal data and data collection parameters for [Zn(4,4′-bpy)(H_2O)$_3$(ClO_4)]-(ClO_4)·(4,4′-bpy)$_{1.5}$·H_2O

Formula	$C_{25}H_{28}Cl_2N_5O_{12}Zn$
Formula weight	726.79
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	9.0187(7)
b (Å)	11.307(2)
c (Å)	16.437(3)
α (°)	74.64(1)
β (°)	83.15(1)
γ (°)	70.88(1)
V (Å^3)	1526.1(4)
Z	2
T (K)	300(2)
$D_{calc.}$ (g cm^{-3})	1.582
F(000)	746
μ(MoKα) (cm^{-1})	10.50
Collection range (°)	$2.58 < 2\theta < 50.10$
Index ranges	$-10 \leq h \leq 10, -12 \leq k \leq 13, 0 \leq l \leq 19$
No. of observations	5419
No. of independent reflections	5419 [$R(int) = 0.0000$)
$R(I > 2\sigma)$ (I)	0.052 (4274 reflections)
R_w	0.133
Goodness-of-fit	1.054

RESULTS AND DISCUSSION

In the IR spectrum, there are several broad bands around 3555, 3436, 3111 and 3058 cm^{-1}, mainly attributed to H-O-H stretching vibrations, suggesting the existance of hydrogen bonding interactions.[9] This is consistent with the results of X-ray analysis. Moreover, the DTA curve of **1** shows two endotherms between 30 and 190°C. This is mirrored in the TGA plot with two weight losses of 2.5% and 7.3%, corresponding to one uncoordinated and three coordinated water molecules, respectively.

The structure of complex **1** is shown in Figure 1. Selected bond distances and angles are listed in Table III. The zinc atom is in an octahedral environment resulting from three aqua ligands, one perchlorate oxygen atoms, and two nitrogen atoms, one from each of two 4,4′-bipyridyl ligands with the nitrogen atoms in the *trans* configuration. The Zn–N distances (Zn–N1 2.103(3), Zn–N2$^{\#1}$ 2.116(3) Å, $^{\#1}x$, $y+1$, z) are slightly shorter than those in square network Zn(II) complexes bridged by coordinated 4,4′-bpy molecules.[1,10] Interestingly, all Zn–Ow distances are not identical: the Zn–O(11) bond distance (2.058(3) Å) is slightly shorter than those of Zn–O(9) and Zn–O(10) (both are 2.083(3) Å), probably due to the *trans* directing influence of the perchlorate group, but all these Zn–Ow distances are shorter

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[Zn(4,4'\text{-bpy})(H_2O)_3(ClO_4)](ClO_4)\cdot(4,4'\text{-bpy})_{1.5}\cdot H_2O$

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*[a]
Zn	3151(1)	7263(1)	2913(1)	34(1)
Cl(1)	1533(2)	8917(1)	8798(1)	78(1)
Cl(2)	2263(1)	6525(1)	5177(1)	47(1)
O(1)	1061(9)	8481(5)	9635(4)	175(3)
O(2)	2637(8)	7985(5)	8516(5)	196(4)
O(3)	1875(10)	10053(5)	8665(4)	169(3)
O(4)	155(9)	9263(7)	8338(5)	184(3)
O(5)	2131(5)	7012(3)	4296(2)	74(1)
O(6)	1762(6)	5419(4)	5428(3)	104(2)
O(7)	1303(5)	7493(4)	5566(3)	101(2)
O(8)	3821(6)	6231(5)	5406(4)	131(2)
O(9)	763(3)	7986(2)	2676(2)	46(1)
O(10)	5414(3)	6515(2)	3369(2)	45(1)
O(11)	3817(4)	7595(3)	1652(2)	58(1)
N(1)	3103(3)	5384(3)	3006(2)	35(1)
N(2)	3160(4)	− 902(3)	2990(2)	37(1)
N(3)	− 2003(4)	5632(4)	12402(2)	63(1)
N(4)	4112(5)	3631(4)	9457(2)	61(1)
N(5)	1650(4)	1181(4)	6260(3)	63(1)
C(1)	4247(5)	4612(4)	2616(3)	47(1)
C(2)	4318(5)	3388(4)	2608(3)	45(1)
C(3)	3139(4)	2878(3)	3033(2)	32(1)
C(4)	3161(4)	1564(3)	3025(2)	32(1)
C(5)	4269(5)	827(4)	2551(3)	44(1)
C(6)	4241(5)	− 385(4)	2554(3)	45(1)
C(7)	2104(4)	− 195(3)	3453(3)	41(1)
C(8)	2056(4)	1018(3)	3488(2)	39(1)
C(9)	1960(4)	3673(3)	3443(2)	37(1)
C(10)	1980(4)	4894(3)	3421(2)	38(1)
C(11)	− 1265(7)	6422(5)	11934(4)	74(2)
C(12)	− 27(7)	6076(5)	11373(3)	69(1)
C(13)	495(5)	4814(4)	11284(2)	45(1)
C(14)	1775(5)	4394(4)	10664(2)	46(1)
C(15)	2440(6)	5244(5)	10119(3)	62(1)
C(16)	3580(6)	4822(5)	9532(3)	65(1)
C(17)	3498(8)	2807(5)	10001(4)	90(2)
C(18)	2361(8)	3126(5)	10601(4)	84(2)
C(19)	− 250(5)	3974(4)	11787(3)	53(1)
C(20)	− 1477(6)	4424(5)	12336(3)	62(1)
C(21)	2509(6)	1920(5)	5853(3)	65(1)
C(22)	3821(6)	1510(4)	5360(3)	57(1)
C(23)	4293(4)	249(4)	5263(2)	43(1)
C(24)	3406(5)	− 526(5)	5693(3)	58(1)
C(25)	2113(6)	− 26(5)	6183(3)	66(1)
OW1	2712(5)	9900(4)	549(3)	99(1)

[a] $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

than those in the 2D square network polymer $[Zn(H_2O)_2(4,4\text{-bpy})_2]SiF_6$ (Zn–Ow 2.132(4) Å].[1] The other perchlorate ion is not coordinated but is linked by weak hydrogen bonds to both uncoordinated water molecules (Owl-Hlb···O1* 3.301 Å, 172.3° $* -x, 2-y, 1-z$; Owl-H1c···O3#

TABLE III Selected bond distances (Å) and angles (°) for $[Zn(4,4'\text{-bpy})(H_2O)_3(ClO_4)](ClO_4)\cdot(4,4'\text{-bpy})_{1.5}\cdot H_2O$

Zn–O(11)	2.058(3)	Zn–O(10)	2.083(3)
Zn–N(1)	2.103(3)	Zn–N(2)$^{\#1}$	2.116(3)
Zn–O(5)	2.329(3)	Zn–O(9)	2.083(3)
O(11)–Zn–O(9)	93.56(13)	O(11)–Zn–O(10)	96.34(12)
O(11)–Zn–N(1)	94.79(11)	O(9)–Zn–N(1)	90.00(11)
O(10)–Zn–N(1)	90.11(11)	O(11)–Zn–N(2)$^{\#1}$	92.46(12)
O(9)–Zn–N(2)$^{\#1}$	90.68(11)	O(10)–Zn–N(2)$^{\#1}$	87.96(11)
N(1)–Zn–N(2)$^{\#1}$	172.66(11)	O(11)–Zn–O(5)	173.99(14)
O(9)–Zn–O(5)	80.53(13)	O(10)–Zn–O(5)	89.56(13)
N(1)–Zn–O(5)	86.33(11)	N(2)$^{\#1}$–Zn–O(5)	86.57(12)
Relevant H bond distances(Å) and angles(°)			
O(9)–H(9c)······N(5)′	2.702(163.3)	O(10)–H(10b)···N(3)″	2.717(176.2)
O(11)–H(11a)···N(4)‴	2.751(176.1)	O(11)–H(11b)···Ow(1)	2.702(155.7)
Ow(1)–H(1b)···O(1)*	3.301(172.3)	Ow(1)–H(1c)···O(3)$^{\#}$	3.222(167.5)
O(9)–H(9b)···O(4)*	3.006(155.7)	O(10)–H(10a)···O(8)‴	3.128(146.6)

Symmetry codes: $^{\#1}x, y+1, z$; $'-x, 1-y, 1-z$; $''1+x, y, -1+z$; $'''1-x, 1-y, 1-z$; $^{\bullet}-x, 2-y, 1-z$; $^{\#}x, y, -1+z$.

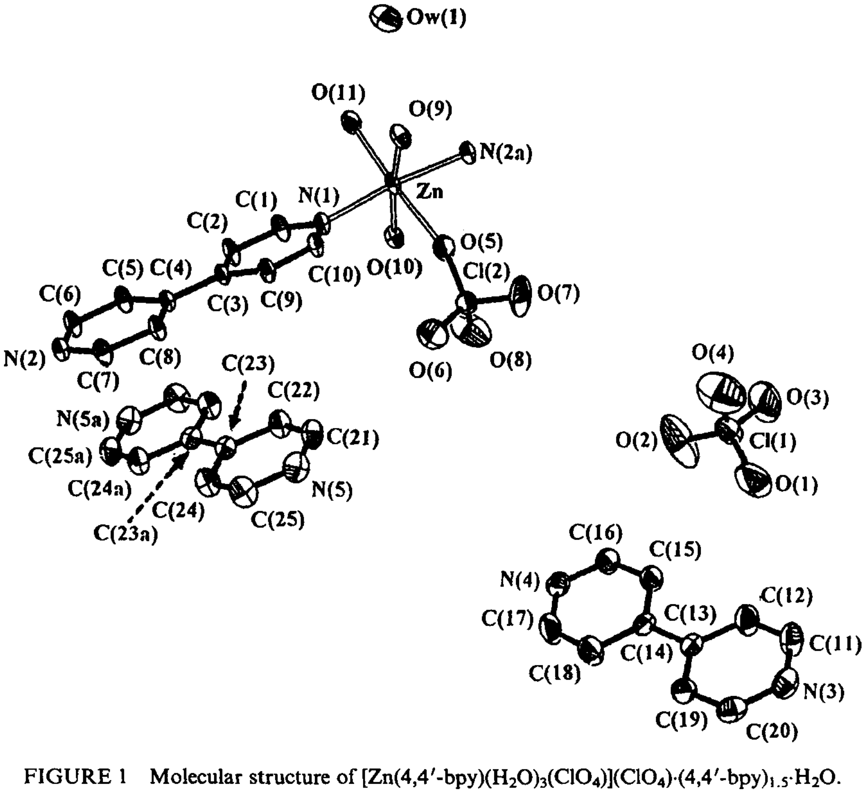

FIGURE 1 Molecular structure of $[Zn(4,4'\text{-bpy})(H_2O)_3(ClO_4)](ClO_4)\cdot(4,4'\text{-bpy})_{1.5}\cdot H_2O$.

3.222 Å, 167.5°, $^{\#}x, y, -1+z$) and a coordinated water molecule (O9-H9b···O4* 3.006 Å, 155.7°, $^{*}-x, 2-y, 1-z$).

As shown in Figure 2, complex 1 consists of one-dimensional chains of zinc ions bridged by coordinated 4,4′-bpy molecules with an intrachain

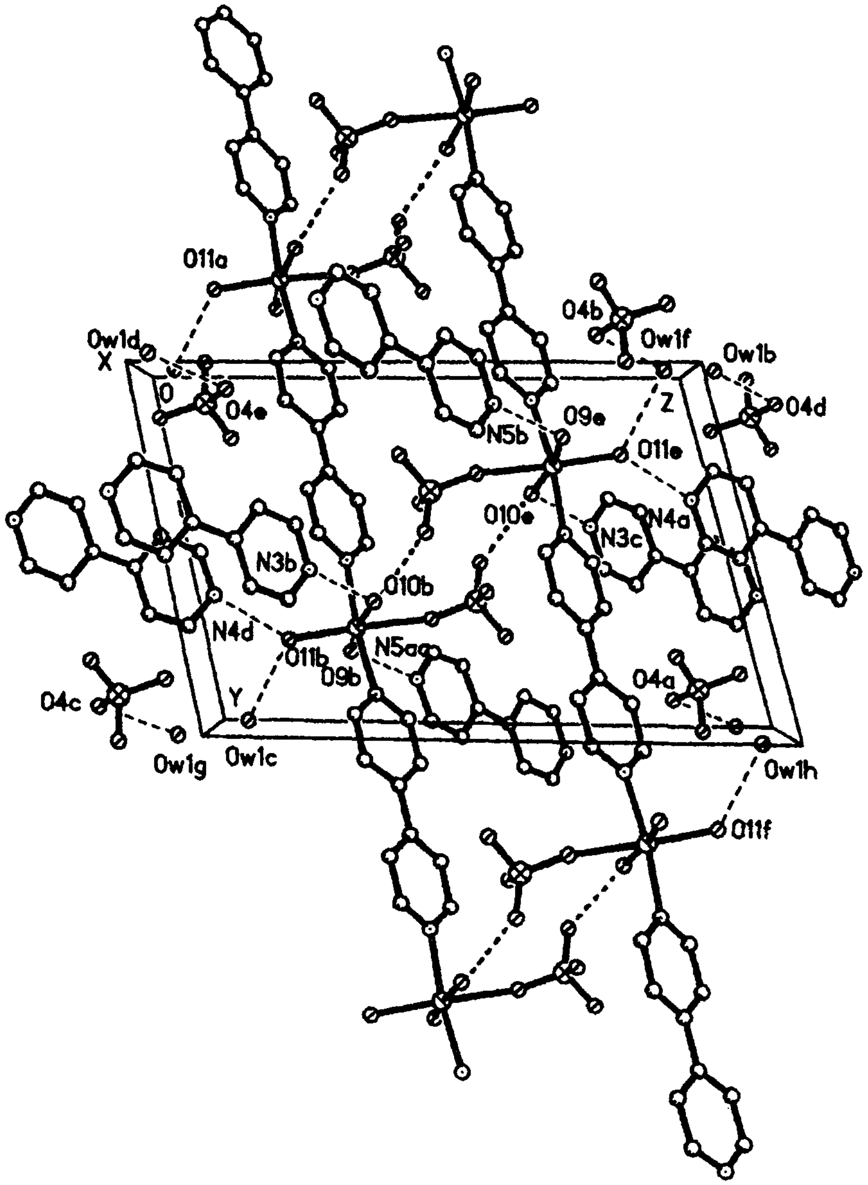

FIGURE 2 Perspective view of the two-dimensional "ladder" structure projected down *a*.

Zn···Zn separation of 11.307 Å running parallel to the *b* axis. The closest Zn–Zn contact is 7.749 Å between neighboring polymeric chains related by a centre of inversion. These two adjacent polymeric chains are interconnected by hydrogen bonds between coordinated water molecules and coordinated perchlorate anions (O10-H10a···O8‴ 3.128 Å, 146.6°, ‴$1-x, 1-y, 1-z$), resulting in a two-dimensional "ladder" parallel to the *b* axis with cavities (7.75 × 11.31 Å). It is novel for hydrogen bonds to interconnect two polymeric chains to form a cavity although similar hydrogen bonds have been found in a 4,4′-bpy copper(II) aqua perchlorate complex, $[Cu(4,4\text{-bpy})(H_2O)_2(ClO_4)_2](4,4'\text{-bpy})$,[11] where each pair of adjacent polymeric chains is interconnected by hydrogen bonds between coordinated aqua ligands and coordinated perchlorate anions, resulting in two-dimensional layers. The main difference between complex **1** and $[Cu(4,4\text{-bpy})(H_2O)_2(ClO_4)_2](4,4'\text{-bpy})$ is that only half of the perchlorate anions in complex **1** but all in the latter are coordinated and connected with adjacent chain water molecules with hydrogen bonds.

Although the nitrogen atoms of a 4,4′-bpy molecule would be expected to have a stronger tendency to bond to the zinc(II) ion in comparison to water molecules and perchlorate anions, uncoordinated 4,4′-bpy molecules exist in the complex. As depicted in Figure 3, these 4,4′-bpy molecules, through hydrogen bonding-interactions, bridge zinc atoms in adjacent chains *via* intermediate water molecules (Zn···Zn^{*1} 15.504(2) Å, bridged by 4,4′-bpy containing N5, $^{*1}-1-x, 2-y, 1-z$; Zn···Zn^{*2} 15.061(2) Å, bridged by 4,4′-bpy containing N3 and N4, $^{*2}2-x, 1-y, -z$). Each one-dimensional chain of $[Zn(4,4'\text{-bpy})(H_2O)_3(ClO_4)]$ is linked by hydrogen bonds to other chains by uncoordinated noncentrosymmetric 4,4′-bpy (O10-H10b···N3″, 2.717 Å, 176.2°, ″$1+x, y, -1+z$, O11-H11a···N4‴, 2.751 Å, 176.1°, ‴$1-x, 1-y, 1-z$) and centrosymmetric 4,4′-bpy (O9-H9c···N5′, 2.702 Å, 163.3°, ′$-x, 1-y, 1-z$). Consequently, The two-dimensional "ladder" structure is extended into a three-dimensional network through these hydrogen bonds. Similar trends have also been observed in another polymeric copper complex, $[Cu(4,4\text{-bpy})(H_2O)_2(BF_4)_2](4,4'\text{-bpy})$,[12] where uncoordinated 4,4′-bpy molecules are used to bridge copper atoms *via* intermediate water molecules.

Because all three water molecules coordinated to zinc atom are hydrogen bonded to uncoordinated 4,4′-bpy molecules acting as bridges to connect adjacent chains, three involving uncoordinated 4,4′-bpy molecules are constrained to locate on two sides of the zinc atom; one uncoordinated 4,4′-bpy molecule is enclosed by the cavity in the "ladder" and its two pyridine rings are required to be coplanar due to the midpoint of the 4,4′-bond being

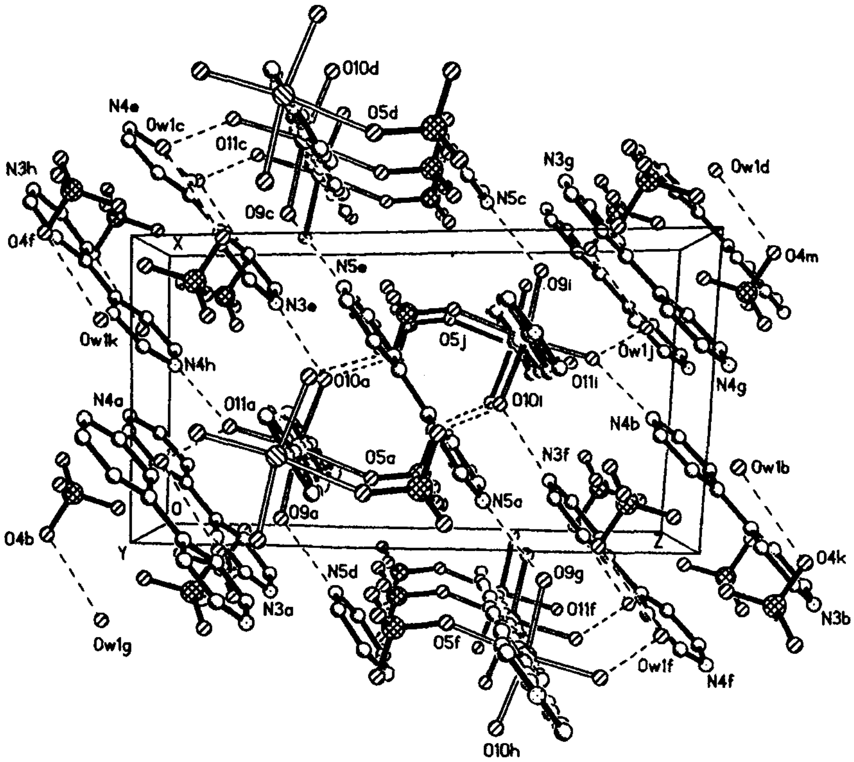

FIGURE 3 Molecular packing of $[Zn(4,4'\text{-bpy})(H_2O)_3(ClO_4)](ClO_4)\cdot(4,4'\text{-bpy})_{1.5}\cdot H_2O$, viewed along the *b* axis, showing 4,4′-bipyridine containing N5 is clathrated in a cavity of the "ladder", whereas 4,4′-bipyridine containing N3 and N4 is intercalated in between "ladder" layers.

located at an inversion centre, whereas the other two on the opposite side of the zinc atom are intercalated in between the "ladder" layers. The column formed is like those of dimethylpyrazine and phenazine intercalated in $\{[Cu(CA)(H_2O)_2]_k\}_l$ layers (H_2CA = chloranilic acid).[13] These two 4,4′-bpy molecules are arranged parallel with an intermolecular nitrogen-nitrogen atom contact N4–N3$*^3$ of 3.557 Å ($*^3 - x, 1-y, 2-z$), indicative of significant π–π stacking interactions between the pyridine rings.[14] They are non-centrosymmetric with an interplanar angle of 5.9°. Furthermore, the coordinated 4,4′-bpy molecule is quite planar; two pyridine rings make a dihedral angle of 5.3°. This arrangement is facilitated by other π–π stacking interactions between coordinated and uncoordinated 4,4′-bpy rings (C19-C9$*^4$ 3.442 Å, $*^4 x, y, 1+z$, C23-C4$*^5$ 3.577 Å, $*^5 1-x, -y, 1-z$). It is worth pointing out that, to our knowledge, this is the first structurally characterized zinc(II) complex of 4,4′-bpy both clathrating and intercalating organic molecules, although clathrations by other transition-metal complexes of 4,4′-bpy have been reported.[4,15,16]

Supplementry material

H atom positions, anisotropic thermal parameters and lists of observed and calculated structures are available from the authors on request.

Acknowledgements

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