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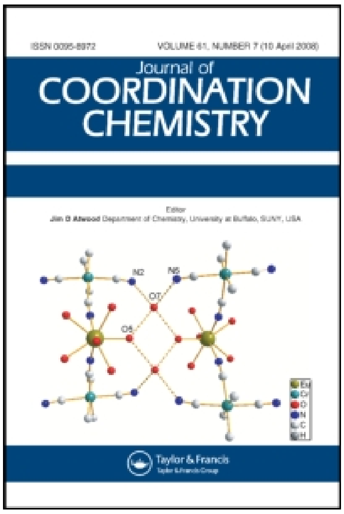

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Syntheses and crystal structures of $[Mn(H_2O)_4(bpy)]L \cdot 4H_2O$, $[Mn(H_2O)_4(bpy)]L' \cdot 4H_2O$ and $[Zn(H_2O)_4(bpy)]L \cdot 4H_2O$ (H_2L = succinic acid, H_2L' = fumaric acid)

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SYNTHESES AND CRYSTAL STRUCTURES OF $[Mn(H_2O)_4(bpy)]L \cdot 4H_2O$, $[Mn(H_2O)_4(bpy)]L' \cdot 4H_2O$ AND $[Zn(H_2O)_4(bpy)]L \cdot 4H_2O$ (H_2L = SUCCINIC ACID, H_2L' = FUMARIC ACID)

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Reactions of freshly prepared $M(OH)_{2-2x}(CO_3)_x \cdot yH_2O$ (M = Mn, Zn) and 4,4′-bipyridine (bpy) with succinic acid (H_2L) or fumaric acid (H_2L') in $CH_3OH–H_2O$ afforded $[Mn(H_2O)_4(bpy)]L \cdot 4H_2O$, **1**, $[Mn(H_2O)_4(bpy)]L' \cdot 4H_2O$, **2** and $[Zn(H_2O)_4(bpy)]L \cdot 4H_2O$, **3**. The three coordination polymers are isostructural and consist of ${}^1_\infty[M(H_2O)_4(bpy)_{2/2}]^{2+}$ cationic chains, crystal H_2O molecules and dicarboxylate anions (succinate or fumarate anions). Within the chains, the metal atoms are each octahedrally coordinated by four aqua oxygen atoms and two pyridyl nitrogen atoms from two 4,4′-bipyridine ligands. The crystal H_2O molecules are hydrogen bonded to dicarboxylate anions to form ribbon-like anionic chains. The cationic and anionic chains are interconnected via hydrogen bonds to generate a 3D network. Crystal data: **1** triclinic, $P\bar{1}$, $a = 7.235(1)$, $b = 7.749(2)$, $c = 10.020(2)$ Å, $\alpha = 79.95(3)$, $\beta = 88.79(3)$, $\gamma = 71.39(3)°$, $V = 523.9(2)$ Å^3 and $D_{cal} = 1.494\ g\,cm^{-3}$ for $Z = 1$; **2** triclinic, $P\bar{1}$, $a = 7.127(1)$, $b = 7.800(2)$, $c = 9.945(2)$ Å, $\alpha = 80.26(3)$, $\beta = 87.86(3)$, $\gamma = 72.69(3)°$, $V = 520.2(2)$ Å^3 and $D_{cal} = 1.498\ g\,cm^{-3}$ for $Z = 1$; **3** triclinic, $P\bar{1}$, $a = 7.189(1)$, $b = 7.764(2)$, $c = 9.843(2)$ Å, $\alpha = 79.16(3)$, $\beta = 87.80(3)$, $\gamma = 71.29(3)°$, $V = 510.9(2)$ Å^3 and $D_{cal} = 1.559\ g\,cm^{-3}$ for $Z = 1$.

Keywords: Mn(II) complex; Zn(II) complex; 4,4′-Bipyridine; Succinato complex; Fumarato complex; Crystal structures

INTRODUCTION

Metal-organic compounds are currently the focus of much interest because of their compositional and structural flexibility in the design of porous crystalline materials [1–7]. Extensive investigations have been carried out, aimed at constructing coordination polymers with open frameworks based on rigid rod-like N-donor bridging ligands such as 4,4′-bipyridine [8–15]. Such compounds present a cationic framework, charge-compensated by small anions in the cavities of the solid. The use of rigid aromatic carboxylate anions to construct neutral open networks has been a main topic of

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current research [16–18]. Recent investigations have focussed on rational design and syntheses of coordination polymers based on simultaneous coordination of rigid 4,4′-bipyridine and flexible aliphatic carboxylates, and the reaction of copper succinate dihydrate ($Cu(C_4H_4O_4)\cdot 2H_2O$), ammonia and 4,4′-bipyridine (bpy) in aqueous methanol yielded an interesting 3D framework coordination polymer $[Cu(H_2O)_2(bpy)(C_4H_4O_4)]\cdot 2H_2O$, where succinato-bridged helical chains are interconnected by 4,4′-bipyridine ligands [19]. Here we report three new compounds, $[Mn(H_2O)_4(bpy)]L\cdot 4H_2O$, **1**, $[Mn(H_2O)_4(bpy)]L'\cdot 4H_2O$, **2** and $[Zn(H_2O)_4(bpy)]L\cdot 4H_2O$, **3** ($H_2L$ = succinic acid, H_2L' = fumaric acid) resulting from reactions of fresh $M(OH)_{2-2x}(CO_3)_x\cdot yH_2O$ (M = Mn, Zn), 4,4′-bipyridine and the corresponding dicarboxylic acids in aqueous methanol.

EXPERIMENTAL

Physical Measurements

All chemicals of *p.a.* grade were commercially available and used without further purification. C, N and H microanalyses were performed with a Perkin Elmer 2400II CHNO/S instrument. FT-IR spectra were recorded using KBr pellets in the range 4000–400 cm^{-1} on a Shimadzu FTIR–8900 spectrophotometer.

Syntheses

$[Mn(H_2O)_4(bpy)](C_4H_4O_4)\cdot 4H_2O$, 1 Dropwise addition of 1.0 cm^3 of 1 M aqueous Na_2CO_3 to a stirred aqueous solution of $MnSO_4\cdot H_2O$ (0.085 g, 0.50 mmol) in 5.0 cm^3 of H_2O produced a pale yellow precipitate, $Mn(OH)_{2-2x}(CO_3)_x\cdot yH_2O$, which was centrifuged and washed with water until no SO_4^{2-} anions were detected in the supernatant. The precipitate was then added to a stirred aqueous methanolic solution of succinic acid (0.059 g, 0.50 mmol) in 20.0 cm^3 CH_3OH–H_2O (1 : 1, v/v). The resulting suspension was mixed with a methanolic solution of 0.096 g (0.50 mmol) of 4,4′-bipyridine · H_2O (bpy · H_2O) in 5.0 cm^3 of CH_3OH. The mixture was further stirred for *ca.* 30 min. Insoluble solids were filtered off, and the colourless filtrate (pH = 6.32) was allowed to stand at room temperature. Slow evaporation during several days afforded yellow crystals. Yield: 70% based on initial $MnSO_4\cdot H_2O$. *Anal.* Calcd. for $C_{14}H_{28}MnN_2O_{12}$(%): C, 35.68; N, 5.99; H, 5.94. Found: C, 35.56; N, 5.90; H, 6.12. IR (cm^{-1}): 3312m, 1602s, 1537vs, 1408s, 1385s, 1340w, 1225m, 1151m, 1057m, 1040w, 1001w, 818s, 802s, 729m, 652m, 620s, 608w, 473w.

$[Mn(H_2O)_4(bpy)](C_4H_2O_4)\cdot 4H_2O$, 2 A synthetic procedure analogous to that used for **1** was employed except that fumaric acid (0.058 g, 0.50 mmol) was used instead of succinic acid. The resulting colourless filtrate was weakly acidic (pH = 5.80) and after several days yielded yellow crystals. Yield: 25% based on the initial $MnSO_4\cdot H_2O$. *Anal.* Calcd. for $C_{14}H_{26}MnN_2O_{12}$(%): C, 35.83; N, 5.97; H, 5.58. Found: C, 35.78; N, 5.96; H, 5.57. IR (cm^{-1}): 3261vs, 1686w, 1609s, 1541vs, 1414m, 1375vs, 1325vw, 1217m, 1154w, 1063m, 1040w, 1007w, 982m, 800s, 725w, 670m, 631m, 590w, 476vw, 449vw.

$[Zn(H_2O)_4(bpy)](C_4H_4O_4)\cdot 4H_2O$, 3 A synthetic procedure analogous to that for **1** was used except that $Zn(NO_3)\cdot 6H_2O$ was used in place of $MnSO_4\cdot H_2O$. Slow evaporation of the colourless filtrate (pH = 5.24) at room temperature during several days gave a few yellowish, needle-like crystals.

X-ray Crystallography

Suitable single crystals of **1**, **2** and **3** were selected under a polarizing microscope and fixed with epoxy cement on fine glass fibres which were mounted on a Bruker P4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) for cell determination and data collection. The lattice parameters were refined from 2θ values (10–25°) of 25 carefully centred reflections and reflection intensities were collected at 293 K using the θ–2θ scan technique. Corrections for Lorentz polarization and absorption effects were performed on the basis of ψ-scans. The structures were solved by direct methods using the SHELXS-97 program [20]. Subsequent difference Fourier syntheses enabled all non-hydrogen atoms to be located. After several cycles of refinement, hydrogen atoms associated with C atoms were added in calculated positions and hydrogen atoms of H_2O molecules were derived from difference Fourier syntheses. Final full-matrix least-squares refinement using the SHELXL-97 program [21] converged very well using anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms. Crystal data, intensity collection and structure refinement details are summarized in Table I, and final non-hydrogen atomic positional parameters for **1**, **2** and **3** are listed in Table II. Selected interatomic distances and bond angles are given in Table III.

TABLE I Crystal data and structure refinement details for **1**, **2** and **3**

	1	*2*	*3*
Empirical formula	$C_{14}H_{28}MnN_2O_{12}$	$C_{14}H_{26}MnN_2O_{12}$	$C_{14}H_{28}N_2O_{12}Zn$
Molecular weight	471.32	469.31	479.74
Description	Yellow prisms	Yellow prisms	Yellow prisms
Crystal size (mm)	0.31 × 0.18 × 0.09	0.31 × 0.22 × 0.16	0.51 × 0.40 × 0.18
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
a (Å)	7.235(1)	7.127(1)	7.189(1)
b (Å)	7.749(2)	7.800(2)	7.764(2)
c (Å)	10.020(2)	9.945(2)	9.843(2)
α (°)	79.95(3)	80.26(3)	79.16(3)
β (°)	88.79(3)	87.86(3)	87.80(3)
γ (°)	71.39(3)	72.69(3)	71.29(3)
Volume (Å^3)	523.9(2)	520.2(2)	510.9(2)
Z	1	1	1
D_{calc} (g cm^{-3})	1.494	1.498	1.559
$F(000)$	247	245	250
μ (mm^{-1})	0.692	0.697	1.266
Absorption correction	Empirical	Empirical	Empirical
θ Range (°)	2.07–27.50	2.08–27.50	2.11–30.00
Refinement method	Full-matrix least-squares on F^2		
Reflections collected	2964	2946	3606
Independent reflections	2394 ($R_{int} = 0.0308$)	2376 ($R_{int} = 0.0246$)	2950 ($R_{int} = 0.0219$)
Data/restraints/parameters	1973/0/191	2179/0/186	2699/0/186
Goodness-of-fit on F^2	1.028	1.058	1.109
R_1, wR_2 [$I \geq 2\sigma(I)$]^a	0.0354, 0.0828	0.0296, 0.0744	0.0334, 0.0915
R_1, wR_2 (all data)^a	0.0478, 0.0882	0.0337, 0.0770	0.0390, 0.0965
Extinction coefficient	0.023(4)	0.046(4)	0.053(6)
Largest diff. peak and hole (e Å^{-3})	0.313, –0.337	0.327, –0.238	0.900, –0.660

$^a wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

TABLE II Atomic parameters and equivalent isotropic thermal parameters (Å^2) for non-hydrogen atoms in **1**, **2** and **3**

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
*Complex **1***				
Mn	0	0	0	0.0252(2)
N(1)	−0.0272(2)	0.1960(2)	−0.1977(2)	0.0297(4)
C(1)	−0.0793(3)	0.3784(3)	−0.2025(2)	0.0343(5)
C(2)	−0.0703(3)	0.5012(3)	−0.3175(2)	0.0336(4)
C(3)	−0.0064(3)	0.4363(3)	−0.4369(2)	0.0257(4)
C(4)	0.0468(3)	0.2471(3)	−0.4312(2)	0.0359(5)
C(5)	0.0346(3)	0.1335(3)	−0.3120(2)	0.0368(5)
O(1)	−0.2711(2)	0.1729(2)	0.0589(2)	0.0427(4)
O(2)	−0.1699(2)	−0.1507(2)	−0.0879(2)	0.0373(4)
O(3)	−0.3497(3)	0.3905(2)	0.2365(2)	0.0517(5)
O(4)	−0.3977(3)	0.2008(2)	0.4163(2)	0.0428(4)
C(6)	−0.4023(3)	0.3569(3)	0.3562(2)	0.0302(4)
C(7)	−0.4760(3)	0.5223(3)	0.4266(2)	0.0259(4)
O(5)	−0.4051(2)	0.7435(3)	0.1124(2)	0.0403(4)
O(6)	−0.5732(3)	−0.0172(2)	0.3133(2)	0.0473(4)
*Complex **2***				
Mn	0	0	0	0.0267(1)
N(1)	−0.0258(2)	0.1954(2)	−0.1970(1)	0.0329(3)
C(1)	−0.0821(3)	0.3751(2)	−0.2004(2)	0.0395(4)
C(2)	−0.0734(3)	0.4978(2)	−0.3159(2)	0.0380(4)
C(3)	−0.0048(2)	0.4356(2)	−0.4366(1)	0.0285(3)
C(4)	0.0519(3)	0.2497(2)	−0.4327(2)	0.0415(4)
C(5)	0.0401(3)	0.1356(2)	−0.3126(2)	0.0410(4)
O(1)	−0.2738(2)	0.1663(2)	0.0643(1)	0.0432(3)
O(2)	−0.1694(2)	−0.1504(2)	−0.0900(1)	0.0393(3)
O(3)	−0.3563(2)	0.3934(2)	0.2387(1)	0.0515(4)
O(4)	−0.3969(2)	0.1957(2)	0.4171(1)	0.0453(3)
C(6)	−0.4007(2)	0.3513(2)	0.3607(2)	0.0333(3)
C(7)	−0.4622(3)	0.5049(2)	0.4402(2)	0.0362(3)
O(5)	−0.4099(2)	0.7422(2)	0.1125(1)	0.0424(3)
O(6)	−0.5763(2)	−0.0207(2)	0.3125(1)	0.0478(3)
*Complex **3***				
Zn	0	0	0	0.0237(1)
N(1)	−0.0244(2)	0.1900(2)	−0.1904(1)	0.0259(3)
C(1)	−0.0778(3)	0.3726(3)	−0.1944(2)	0.0301(4)
C(2)	−0.0700(3)	0.4979(2)	−0.3128(2)	0.0302(4)
C(3)	−0.0065(2)	0.4353(2)	−0.4351(2)	0.0234(3)
C(4)	0.0462(3)	0.2457(3)	−0.4309(2)	0.0316(4)
C(5)	0.0360(3)	0.1293(2)	−0.3077(2)	0.0317(4)
O(1)	−0.2700(2)	0.1616(2)	0.0612(2)	0.0359(3)
O(2)	−0.1579(2)	−0.1488(2)	−0.0891(2)	0.0324(3)
O(3)	−0.3479(3)	0.3955(2)	0.2298(2)	0.0482(4)
O(4)	−0.3994(3)	0.2031(2)	0.4128(2)	0.0414(4)
C(6)	−0.4021(3)	0.3598(2)	0.3522(2)	0.0284(3)
C(7)	−0.4766(3)	0.5240(2)	0.4247(2)	0.0243(3)
O(5)	−0.4063(3)	0.7513(3)	0.1089(2)	0.0372(3)
O(6)	−0.5761(3)	−0.0169(2)	0.3136(2)	0.0432(4)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

RESULTS AND DISCUSSION

Shi and coworkers [22] have isolated two Mn coordination polymers containing both dicarboxylate and 4,4′-bipyridine bridging ligands by reaction of dicarboxylic acids, $MnCl_2 \cdot 4H_2O$ and 4,4′-bipyridine $\cdot\, 2H_2O$ in mixed H_2O and methanol. However, the

TABLE III Selected interatomic distances (Å) and bond angles (°) for **1**, **2** and **3**

	1	*2*	*3*	
M–O(1)	2.131(2)	2.140(1)	2.066(2)	
M–O(2)	2.230(2)	2.217(1)	2.166(2)	
M–N(1)	2.246(2)	2.246(1)	2.131(2)	
N(1)–C(1)	1.334(3)	1.333(2)	1.338(2)	
N(1)–C(5)	1.334(3)	1.330(2)	1.334(2)	
C(1)–C(2)	1.375(3)	1.377(2)	1.383(2)	
C(2)–C(3)	1.391(3)	1.389(2)	1.389(2)	
C(3)–C(4)	1.382(3)	1.379(2)	1.390(2)	
C(3)–C(3)[#2]	1.484(3)	1.486(3)	1.489(3)	
C(4)–C(5)	1.374(3)	1.380(2)	1.384(2)	
O(3)–C(6)	1.260(3)	1.256(2)	1.261(2)	
O(4)–C(6)	1.244(2)	1.241(2)	1.245(2)	
C(6)–C(7)	1.512(3)	1.495(2)	1.516(2)	
C(7)–C(7)[#3]	1.511(4)	1.288(3)	1.511(3)	
O(1)–M–O(2)	87.25(7)	87.70(4)	87.99(7)	
O(1)–M–O(1)[#1]	180	180	180	
O(1)–M–N(1)	90.11(7)	90.00(6)	90.79(7)	
O(2)–M–O(2)[#1]	180	180	180	
O(2)–M–N(1)	90.97(6)	90.51(5)	91.04(6)	
N(1)–M–N(1)[#1]	180	180	180	
Hydrogen bonding contacts for ***1/2/3***				
D–H···A	*d(D–H)*	*d(H···A)*	*d(D–H···A)*	*∠(D–H···A)*
O(1)–H(1A)···O(3)	0.81/0.86/0.80	1.79/1.75/1.80	2.593/2.615/2.602	179/179/174
O(1)–H(1B)···O(5)[#4]	0.81/0.80/0.76	1.96/1.96/2.01	2.769/2.756/2.763	176/177/175
O(2)–H(2A)···O(6)[#5]	0.84/0.81/0.77	1.97/1.99/2.04	2.803/2.797/2.806	172/174/172
O(2)–H(2B)···O(5)[#6]	0.78/0.82/0.75	2.01/1.97/2.02	2.788/2.779/2.763	175/174/174
O(5)–H(3A)···O(6)[#7]	0.90/0.83/0.81	2.07/2.10/2.13	2.954/2.923/2.924	170/170/171
O(5)–H(3B)···O(3)	0.81/0.78/0.73	1.89/1.94/1.98	2.706/2.817/2.698	175/175/167
O(6)–H(4A)···O(4)[#8]	0.84/0.79/0.80	2.05/2.06/2.05	2.870/2.830/2.835	164/164/173
O(6)–H(4B)···O(4)	0.87/0.88/0.89	1.89/1.88/1.88	2.750/2.746/2.757	170/169/168

M = Mn **1**, **2**; M = Zn **3**.
Symmetry codes: [#1] $-x, -y, -z$; [#2] $-x, -y+1, -z-1$; [#3] $-x-1, -y+1, -z+1$; [#4] $-x-1, -y+1, -z$; [#5] $-x-1, -y, -z$; [#6] $x, y-1, z$; [#7] $x, y+1, z$; [#8] $-x-1, -y, -z+1$.

reaction using fresh $M(OH)_{2-2x}(CO_3)_x \cdot yH_2O$ (M = Mn, Zn) instead of $MnCl_2 \cdot 4H_2O$ produced 4,4′-bipyridine-bridged coordination polymers with the dicarboxylate anions non-coordinating. The present reactions could be simply formulated as follows.

$$M^{2+} + L^{2-} + \mathrm{bpy} + 8H_2O \rightarrow [M(H_2O)_4(\mathrm{bpy})]L \cdot 4H_2O$$

This suggests that the product is M^{2+} (M = Mn, Zn) source-dependent, but the reason for this is not clear.

The three compounds isolated are isostructural and consist of 4,4′-bipyridine (bpy)-bridged complex cationic chains formulated as ${}_{\infty}^{1}[M(H_2O)_4(\mathrm{bpy})_{2/2}]^{2+}$ (M = Mn for **1** and **2**, Zn for **3**), crystal H_2O molecules and dicarboxylate anions (succinate for **1** and **3**, fumarate for **2**). As demonstrated in Fig. 1, the metal atoms are each coordinated by four aqua oxygen atoms and two pyridyl nitrogen atoms of two symmetry-related 4,4′-bipyridine ligands to complete slightly elongated octahedra with the oxygen atoms at the equatorial sites. The metal–oxygen bond distances are 2.131, 2.230 Å for **1**, 2.140, 2.217 Å for **2** and 2.066, 2.166 Å for **3**; metal–nitrogen bond lengths are

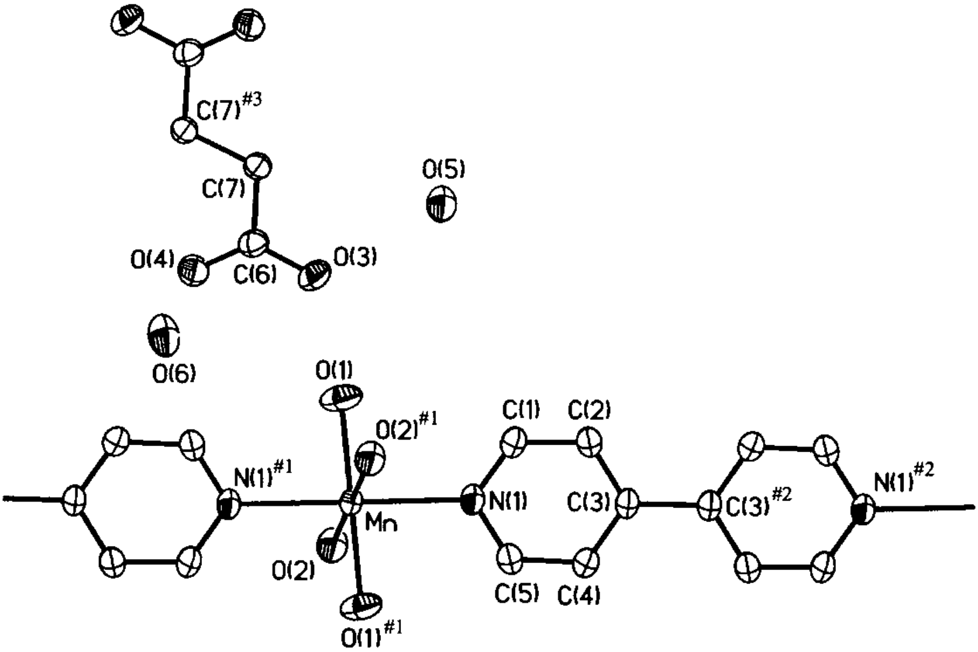

FIGURE 1 ORTEP view of the $_{\infty}^{1}[Mn(H_2O)_4(bpy)_{2/2}]^{2+}$ cationic chain with the succinate anion and crystal water molecules with displacement ellipsoids (50% probability) and atomic labelling in **1**.

2.246, 2.246 and 2.131 Å for **1**, **2** and **3**, respectively (Table III). The *cisoid* bond angles at the metal atom exhibit slight deviations from 90° and the *transoid* ones are equal to 180° due to the local $\bar{1}$ symmetric imposition (Table III). The cationic chains along $[01\bar{1}]$ are arranged in a layer parallel to (100) (Fig. 2). Of the two crystallographically distinct crystal H_2O molecules, one donates two hydrogen atoms to two oxygen atoms of different dicarboxylate anions to form hydrogen bonds and the other is hydrogen bonded to the former water molecule and to one carboxylate oxygen atom, thus leading to one-dimensional, ribbon-like, hydrogen-bonded anionic chains extending in the [010] direction (Fig. 2). Cationic and anionic layers are stacked alternately along [100] (Fig. 3). The cationic and anionic chains are thus interlinked to generate a 3D network.

Except for one band found at 1686 cm^{-1} for **2** due to the C=C double bond [23], **1** and **2** display similar IR spectra, suggesting them to be isostructural, in accordance with the above structure description. Absorption at 3312 and 3261 cm^{-1} for **1** and **2**, respectively, is characteristic of H_2O molecules. The asymmetric $-CO_2$ stretching vibration of the dicarboxylate anions results in strong bands centred at 1537 and 1541 cm^{-1} for **1** and **2**, respectively, while the symmetric $-CO_2$ stretching vibration causes a strong sharp absorption at 1385 and 1375 cm^{-1} for **1** and **2** [24]. Peaks at 1151 and 1154 cm^{-1} for **1** and **2**, respectively, could be assigned to the asymmetric C–C vibration of the dicarboxylate anions. In comparison with 4,4′-bipyridine, vibrations associated with the pyridyl ligands cause absorptions at 1602, 1408, 1340, 1225, 1057, 1040, 818, 802, 729, 608, 473 cm^{-1} for **1** and at 1609, 1414, 1325, 1217, 1063, 1040, 800, 725, 590, 476 cm^{-1} for **2**. Absorption bands due to metal–oxygen bonding are found at 652, 620 cm^{-1} for **1** and at 670, 631 cm^{-1} for **2** [25].

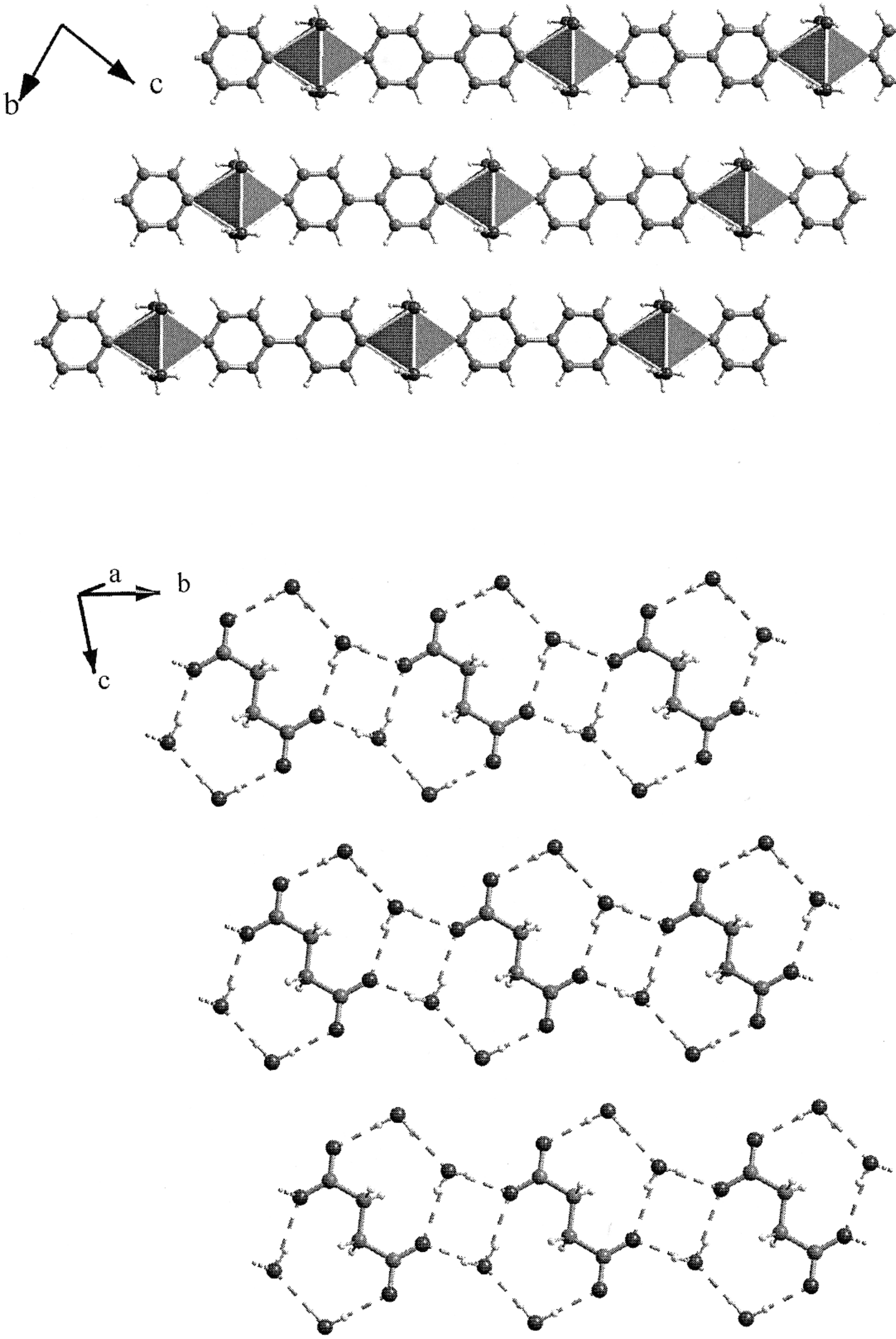

FIGURE 2 Arrangement of the $_{\infty}^{1}[Mn(H_2O)_4(bpy)_{2/2}]^{2+}$ cationic chains (top) and the hydrogen-bonded ribbon like chains composed of succinate anions and crystal water molecules in **1** (bottom).

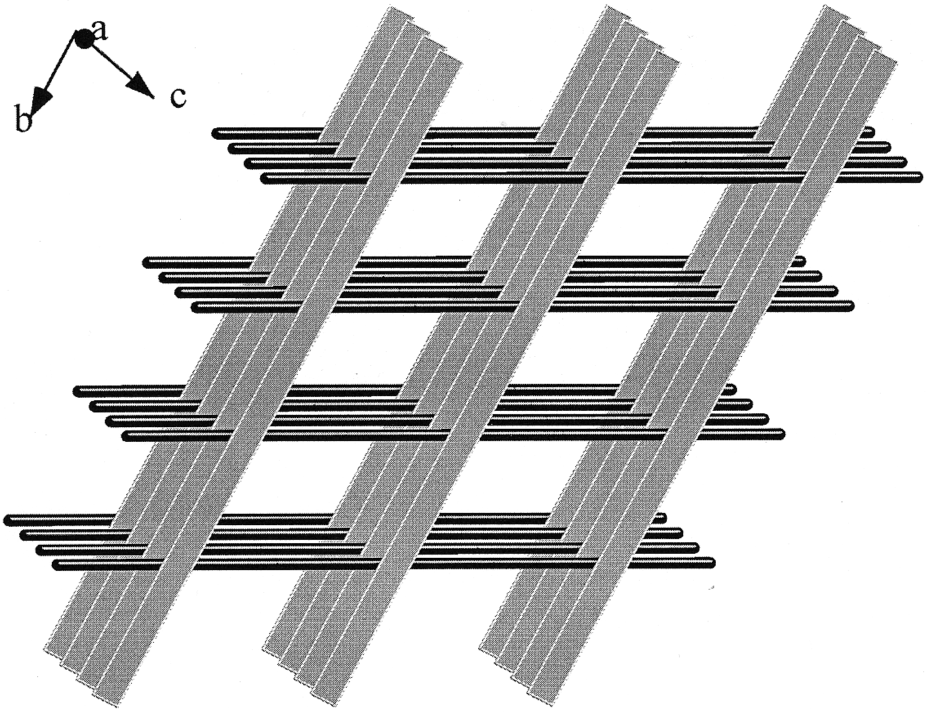

FIGURE 3 Scheme for the assembly of $_{\infty}^{1}[Mn(H_2O)_4(bpy)_{2/2}]^{2+}$ cationic chains (dark rods) and hydrogen-bonded, ribbon-like, anionic chains (gray bands) in **1**.

Acknowledgments

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Supplementary Data

Crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 237628 ($C_{14}H_{28}MnN_2O_{12}$ **1**), CCDC 237629 ($C_{14}H_{26}MnN_2O_{12}$ **2**) and CCDC 237630 ($C_{14}H_{28}N_2O_{12}Zn$ **3**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (Fax: +44 1223 336033 or E-mail: deposit@ccdc.cam.ac.uk).

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