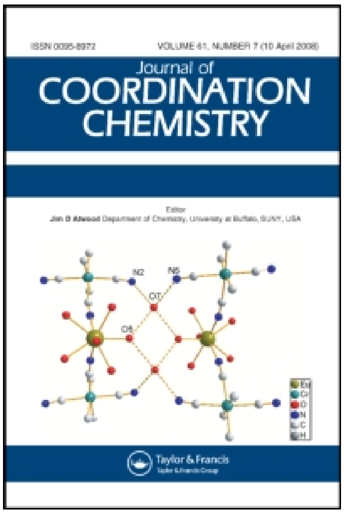

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Syntheses and structures of M-Na (M=Zn, Mn) coordination polymers in which ligands and Na ions exhibit complex coordination modes

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Syntheses and structures of M–Na (M = Zn, Mn) coordination polymers in which ligands and Na ions exhibit complex coordination modes

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The novel heteronuclear complexes $[Na_2Zn(dipic)_2(H_2O)]_n$ (**1**) and $[Na_2Mn(dipic)_2(H_2O)_2]_n$ (**2**) (H_2dipic = pyridine-2,6-dicarboxylic acid) were synthesized and characterized by single-crystal X-ray diffraction, analysis, IR spectroscopy and thermogravimetric analysis. Complex **1** consists of infinite 2D double layers, which are further attached into a 3D network through π–π stacking. All sodium ions are 3-coordinate. Complex **2** has an intricate 3D structure, in which two sodium ions are differently involved in forming polymeric coordination units, and are 3- and 7-coordinate, respectively. Dipic anions act as multidentate ligands showing novel and unprecedented bridging coordination modes. One ligand coordinates to three metal ions and with five bonds; the other coordinates five metal ions with nine bonds.

Keywords: Heteronuclear complex; Multidimensional structure; Sodium, Zinc; Manganese; Pyridine-2,6-dicarboxylic acid; Coordination mode

1. Introduction

Construction of metal–organic polymers based on coordinative covalent bonding has been studied extensively for the interest of potential photoelectric, magnetic, spectral and redox functions in recent years [1–5]. Although, it is not yet possible to prepare fully predictable metal–organic frameworks on the basis of rational design, recent exciting developments in coordination and organic chemistry provide great possibilities for the creative synthesis of desired novel frameworks [6–11].

H_2dipic is an efficient ligand with three coordinating sites. Some polymeric structures of dipic complexes with transition and lanthanide metals have been reported, in which dipic ligand has shown not only the strong chelating ability, but also the bridging tendency to form diversified structures [12–18]. In this research, we obtained two hetero-nuclear complexes with the participation of sodium ion in coordination with dipic ligand and water molecule, which is rather unusually discovered in such a system. In these complexes, dipic ligands coordinate to several metal ions and give further coordination sites, thus construct complicated multi-dimension structures.

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2. Experimental

2.1. *Materials and physical measurements*

Zinc(II) perchlorate hexahydrate and manganese(II) perchlorate hexahydrate were prepared by literature methods [19]. Other reagents were of analytical grade, obtained from commercial sources and used without further purification. IR spectra were recorded in the 400–4000 cm^{-1} range on a Nicolet Impact 410FTIR spectrophotometer using KBr pellets. Elemental analyses were performed on a Perkin-Elmer 2400 instrument. ICP analyses were carried out using a Perkin-Elmer Optima 3300DV ICP instrument. Thermogravimetric analyses (TGA) were carried out on a Perkin-Elmer TGA 7 system under an N_2 atmosphere with a heating rate of 10°C min^{-1}.

2.2. *$[Na_2Zn(dipic)_2(H_2O)]_n$ (1)*

An aqueous solution (15 cm^3) of pyridine-2,6-dicarboxylic acid (0.4 mmol, 66.9 mg) was mixed with 20 cm^3 of a methanol solution of $Zn(ClO_4)_2 \cdot 6H_2O$ (0.4 mmol, 148.8 mg) followed by addition of a concentrated solution of sodium azide (0.8 mmol, 52 mg). The final clear mixture was left to stand at room temperature and colourless blocky crystals were separated out after several days. The crystals were collected at the pump and air-dried. Yield: 20%. Anal. Calcd for **1** (%): Na, 10.01; Zn, 14.23; C, 36.56; H, 1.74; N, 6.09. Found: Na, 10.21; Zn, 14.02; C, 36.39; H, 1.81; N, 5.99.

2.3. *$[Na_2Mn(dipic)_2(H_2O)_2]_n$ (2)*

Some 66.9 mg of pyridine-2,6-dicarboxylic acid (0.4 mmol) was dissolved in 15 cm^3 of water and 144.8 mg $Mn(ClO_4)_2 \cdot 6H_2O$ (0.4 mmol) added to obtain a colourless solution. Then 32 mg (0.8 mmol) NaOH was added to deprotonate H_2dipic. A colourless precipitate formed immediately and 20 cm^3 of DMF was added to dissolve it. After 1 h, the mixture was filtered and the final solution allowed to evaporate slowly at room temperature. Three months later, pink blocky crystals had separated out from solution. Yield: 10%. Anal. Calcd for **2** (%): Na, 9.85; Mn, 11.76; C, 35.96; H, 2.14; N, 5.99. Found: Na, 9.93; Mn, 11.71; C, 35.64; H, 2.03; N, 5.81.

2.4. *Structure determination*

Room temperature (294 ± 1 K) single-crystal X-ray experiments for **1** and **2** were performed on a Bruker SMART 1000 CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation. Data collection and reduction were performed using SMART and SAINT software. An empirical absorption correction (SADABS) was applied to raw intensities. The structures were solved by direct methods and refined by full-matrix least-squares techniques based on F^2 using the SHELXTL program package. Non-hydrogen atoms were subjected to anisotropic refinement. H atoms were assigned common isotropic displacement factors and included in the final refinement by use of geometrical restraints. Crystal data and structure refinement parameters for **1** and **2** are listed in table 1. Selected bond lengths and angles are listed in tables 2 and 3.

Table 1. Crystal data and structure refinement details for **1** and **2**.

	1	**2**
Molecular formula	$C_{14}H_8N_2Na_2O_9Zn$	$C_{14}H_{10}MnN_2Na_2O_{10}$
Molecular weight	459.57	467.16
Colour and habit	Colourless, blocky	Pink, blocky
Crystal size (mm^3)	0.26 × 0.16 × 0.16	0.24 × 0.18 × 0.16
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pna2_1$
a (Å)	14.056(2)	7.912(3)
b (Å)	10.0588(17)	13.603(4)
c (Å)	13.790(2)	15.162(5)
β (°)	116.572(2)	
V ($Å^3$)	1743.8(5)	1631.9(9)
Z	4	4
Density (Calcd) ($g\,cm^{-3}$)	1.751	1.901
Reflections measured/unique	9944/3584	8745/3211
Absorption coefficient (mm^{-1})	1.512	0.927
λ (Å)	0.71073	0.71073
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0492$, $wR_2 = 0.1320$	$R_1 = 0.0325$, $wR_2 = 0.0590$
R indices (all data)	$R_1 = 0.0682$, $wR_2 = 0.1534$	$R_1 = 0.0470$, $wR_2 = 0.0632$
GOF	1.028	0.992

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

Zn(1)–N(1)	2.009(3)	Zn(1)–N(2)	2.013(3)
Zn(1)–O(5)	2.079(3)	Zn(1)–O(1)	2.116(3)
Zn(1)–O(3)	2.320(3)	Zn(1)–O(7)	2.351(3)
O(1)–C(1)	1.278(6)	O(1)–Na(2)	2.671(5)
O(2)–C(1)	1.221(5)	O(3)–C(7)	1.229(5)
O(4)–C(7)	1.292(5)	O(4)–Na(1)	2.482(5)
O(5)–C(8)	1.266(5)	O(6)–C(8)	1.238(5)
O(6)–Na(1)#1	2.710(5)	O(6)–Na(1)#2	2.752(5)
O(7)–C(14)	1.232(5)	O(8)–C(14)	1.286(5)
O(8)–Na(2)#3	2.465(5)	Na(2)–O(9′)#8	2.539(14)
Na(2)–O(9)#8	2.707(11)		
N(1)–Zn(1)–N(2)	166.46(12)	N(1)–Zn(1)–O(5)	113.74(12)
N(2)–Zn(1)–O(5)	79.42(12)	N(1)–Zn(1)–O(1)	78.31(13)
N(2)–Zn(1)–O(1)	104.02(12)	O(5)–Zn(1)–O(1)	97.31(12)
N(1)–Zn(1)–O(3)	74.03(11)	N(2)–Zn(1)–O(3)	102.78(11)
O(5)–Zn(1)–O(3)	94.18(11)	O(1)–Zn(1)–O(3)	152.34(11)
N(1)–Zn(1)–O(7)	93.50(11)	N(2)–Zn(1)–O(7)	73.19(11)
O(5)–Zn(1)–O(7)	152.50(11)	O(1)–Zn(1)–O(7)	91.61(12)
O(3)–Zn(1)–O(7)	89.65(11)	C(9)–N(2)–Zn(1)	115.7(2)
C(13)–N(2)–Zn(1)	123.5(3)	O(2)–C(1)–O(1)	127.2(5)
O(2)–C(1)–C(2)	117.6(5)	O(1)–C(1)–C(2)	115.2(4)
O(4)–Na(1)–O(6)#4	129.38(17)	O(4)–Na(1)–O(6)#5	122.53(16)
O(6)#4–Na(1)–O(6)#5	85.74(13)	O(4)–Na(1)–Na(2)#6	67.61(13)
O(8)#7–Na(2)–O(9′)#8	95.3(3)	O(8)#7–Na(2)–O(1)	115.22(17)
O(9′)#8–Na(2)–O(1)	127.3(4)	O(8)#7–Na(2)–O(9)#8	110.1(4)
O(1)–Na(2)–O(9)#8	101.9(3)		

Symmetry transformations used to generate equivalent atoms are #1: $x, -y+1/2, z+1/2$; #2: $-x, y+1/2, -z+1/2$; #3: $x, -y+3/2, z-1/2$; #4: $x, -y+1/2, z-1/2$; #5: $-x, y-1/2, -z+1/2$; #6: $x, y-1, z$; #7: $x, -y+3/2, z+1/2$; #8: $-x+1, -y+2, -z+1$.

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Mn(1)–N(1)	2.150(2)	Mn(1)–N(2)	2.166(2)
Mn(1)–O(5)	2.192(2)	Mn(1)–O(3)	2.222(3)
Mn(1)–O(1)	2.252(2)	Mn(1)–O(7)	2.266(2)
Na(1)–O(9)	2.291(2)	Na(1)–O(10)	2.395(3)
Na(1)–O(8)#1	2.450(3)	Na(1)–O(2)	2.453(3)
Na(1)–O(8)#2	2.477(3)	Na(2)–O(10)#4	2.343(3)
Na(2)–O(9)	2.394(3)	Na(2)–O(6)#3	2.433(3)
Na(2)–O(5)#3	2.446(3)	Na(2)–O(8)#2	2.617(3)
Na(2)–O(7)#2	2.620(3)	Na(2)–O(2)	2.810(3)
O(1)–C(6)	1.277(4)	O(2)–C(6)	1.239(4)
O(3)–C(7)	1.272(4)	O(4)–C(7)	1.239(4)
O(5)–C(13)	1.271(4)	O(6)–C(13)	1.225(4)
O(7)–C(14)	1.268(3)	O(8)–C(14)	1.251(3)
N(1)–Mn(1)–N(2)	173.06(10)	N(1)–Mn(1)–O(5)	105.23(9)
N(2)–Mn(1)–O(5)	72.75(9)	N(1)–Mn(1)–O(3)	73.01(8)
N(2)–Mn(1)–O(3)	100.70(9)	O(5)–Mn(1)–O(3)	101.32(8)
N(1)–Mn(1)–O(1)	72.05(8)	N(2)–Mn(1)–O(1)	114.12(8)
O(5)–Mn(1)–O(1)	86.53(9)	O(3)–Mn(1)–O(1)	145.03(8)
N(1)–Mn(1)–O(7)	110.26(8)	N(2)–Mn(1)–O(7)	71.71(8)
O(5)–Mn(1)–O(7)	144.42(8)	O(3)–Mn(1)–O(7)	86.81(9)
O(1)–Mn(1)–O(7)	106.53(8)	O(9)–Na(1)–O(10)	154.80(11)
O(9)–Na(1)–O(8)#2	80.97(9)	O(10)–Na(1)–O(8)#2	92.08(8)
O(9)–Na(1)–O(2)	86.91(9)	O(10)–Na(1)–O(2)	91.91(8)
O(8)#2–Na(1)–O(2)	159.43(10)	O(9)–Na(1)–O(8)#2	81.82(9)
O(10)–Na(1)–O(8)#1	122.81(9)	O(8)#1–Na(1)–O(8)#2	113.92(9)
O(2)–Na(1)–O(8)#2	80.38(8)	O(10)#4–Na(2)–O(9)	163.27(9)
O(10)#4–Na(2)–O(6)#3	103.96(9)	O(9)–Na(2)–O(6)#3	92.76(8)
O(10)#4–Na(2)–O(5)#3	113.75(10)	O(9)–Na(2)–O(5)#3	75.87(9)
O(6)#3–Na(2)–O(5)#3	54.05(8)	O(10)#4–Na(2)–O(8)#2	89.19(8)
O(9)–Na(2)–O(8)#2	77.03(8)	O(6)#3–Na(2)–O(8)#2	144.51(9)
O(5)#3–Na(2)–O(8)#2	147.86(10)	O(10)#4–Na(2)–O(7)#2	99.91(9)
O(9)–Na(2)–O(7)#2	78.70(8)	O(6)#3–Na(2)–O(7)#2	94.53(8)
O(5)#3–Na(2)–O(7)#2	137.69(10)	O(8)#2–Na(2)–O(7)#2	50.35(7)
O(10)#4–Na(2)–O(2)	89.52(9)	O(9)–Na(2)–O(2)	77.26(8)
O(6)#3–Na(2)–O(2)	139.73(9)	O(5)#3–Na(2)–O(2)	85.72(9)
O(8)#2–Na(2)–O(2)	71.67(7)	O(7)#2–Na(2)–O(2)	120.69(8)
O(4)–C(7)–O(3)	126.1(3)	O(2)–C(6)–O(1)	125.5(3)
O(8)–C(14)–O(7)	124.3(3)	O(6)–C(13)–O(5)	125.3(3)

Symmetry transformations used to generate equivalent atoms are #1: $-x+1$, $-y+2$, $z-1/2$; #2: $-x+3/2$, $y-1/2$, $z-1/2$; #3: $x-1/2$, $-y+3/2$, z; #4: $x+1/2$, $-y+3/2$, z.

3. Results and discussion

3.1. *IR spectra*

The salient feature of the IR spectrum of **1** is the existence of strong bands at 1661, 1628, 1576, and 1367 cm^{-1}, attributed to ν(C=O) and ν(C–O), respectively. A weak peak at 1593 cm^{-1} is assigned to absorption of C=N group. In **2**, features at 1653, 1620, 1576, and 1358 cm^{-1} are assigned to ν(C=O) and ν(C–O), respectively, and that at 1600 cm^{-1} to absorption of the C=N group.

3.2. *Crystal structure of* $[Na_2Zn(dipic)_2(H_2O)]_n$ *(1)*

The crystal structure of **1**, as depicted in figure 1, consists of the polymeric unit $[Na_2Zn(dipic)_2(H_2O)]_n$, which contains six-coordinate Zn^{2+} ion and two

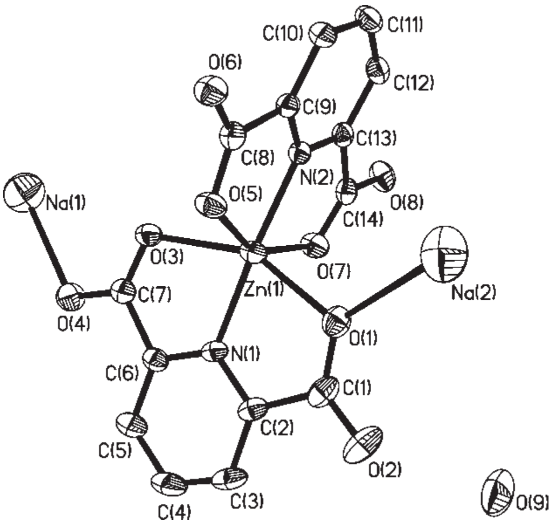

Figure 1. An ORTEP drawing of **1** with 30% probability ellipsoids showing the atom numbering scheme.

three-coordinate Na^+ ions. Zinc(II) lies in a distorted octahedral environment with a ZnN_2O_4 core involving four oxygen and two nitrogen atoms from two dipic dianions. There are two crystallographic independent sodium cations, which exhibit different coordination environments. The first is coordinated by three oxygen atoms from three different dipic ligands (Na–O bond lengths vary from 2.482(5) to 2.752(5) Å), while the other is coordinated by three oxygen atoms from two dipic ligands and a coordinated water (Na–O bond lenths vary from 2.465(5) to 2.707(11) Å). The dipic dianions act as multidentate ligands bridging zinc and sodium ions. One dipic ligand connects two sodium ions and the other connects three.

Figure 2, omitting some non-essential atoms, shows the 2D network of **1**. The bi-layer structure is comprised of cycles involving eight metals extending in two different directions (figure 2(a); four Zn^{2+} and four Na^+ ions), forming knots in the network. Each Zn^{2+} ion is connected to four Na^+ ions through three carboxylate groups and one carboxylate oxygen atom and each Na^+ ion is linked to two Zn^{2+} ions in two ways. Mode **I** links through two carboxylate groups and mode **II** links through a carboxylate group and a carboxylate oxygen atom. Sodium ions of mode **I** connect with zinc ions in another layer through a carboxylate group to give the bi-layer structure (figure 2b). Dipic rings of neighbouring bi-layers interdigitate, as shown in figure 3, and there are face-to-face π–π stacking interactions between dipic rings, forming a 3D assembly. The distance between dipic rings is ca 3.30 Å.

3.3. *Crystal structure of* $[Na_2Mn(dipic)_2(H_2O)_2]_n$ *(2)*

The crystal structure of **2**, as depicted in figure 4, contains the polymeric unit $[Na_2Mn(dipic)_2(H_2O)_2]_n$, which consists of one six-coordinate Mn^{2+} ion and two multi-coordinate Na^+ ions. One Na^+ ion is five-coordinate to three carboxylate oxygen atoms of three different dipic dianions and two oxygen atoms of water, forming

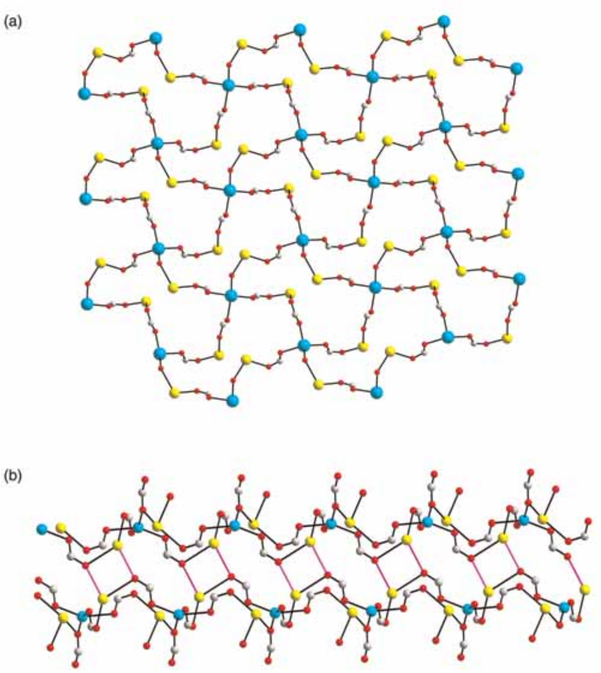

Figure 2. Packing views of **1**; (a) single-layer structure, (b) bi-layer structure. Color scheme: zinc, cyan; sodium, yellow; oxygen, red; carbon, gray. Purple lines emphasize the connections between the monolayers.

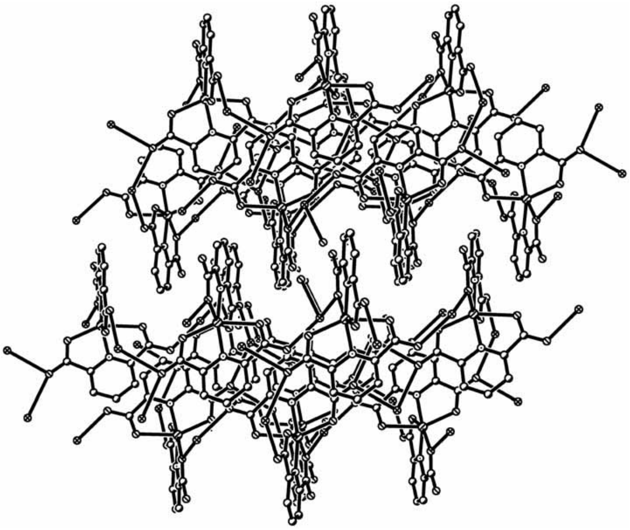

Figure 3. Packing view of **1** highlighting π–π stacking interactions between layers.

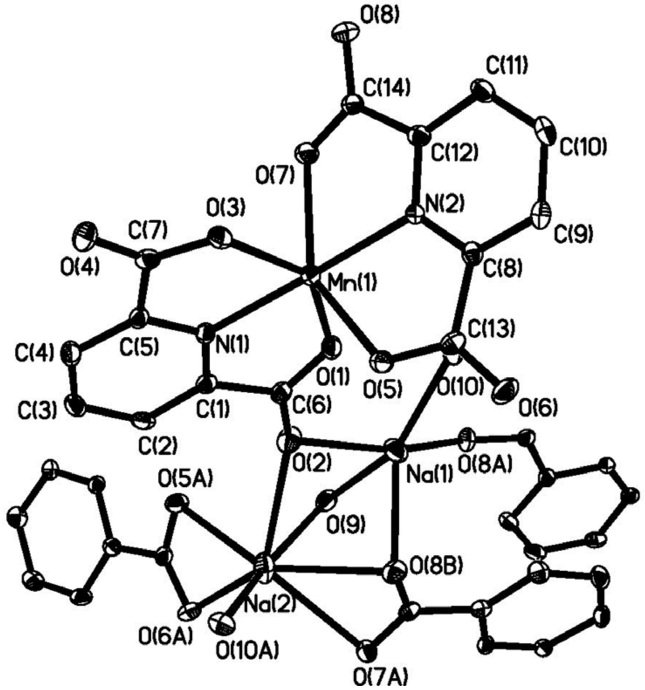

Figure 4. An ORTEP drawing of $[Na_2Mn(dipic)_2(H_2O)_2]_n$ with 30% probability ellipsoids showing the atom numbering scheme.

a distorted trigonal bipyramid coordination polyhedron. The three Na–O (dipic) bond lengths (2.450(3), 2.453(3) and 2.477(3) Å) are longer than those of the coordinated water molecules (2.291(2) and 2.395(3) Å). The other Na^+ ion is seven-coordinate to five carboxylate oxygen atoms of three different dipic dianions and two oxygen atoms of water, forming a distorted pentagonal bipyramid polyhedron. The five Na–O (dipic) bond lengths vary from 2.433(3) to 2.810(3) Å, indicating considerable distotion caused by the asymmetric coordination modes of the dipic ligands. Bond distances Na–O (water) are also much shorter (2.343(3) and 2.394(3) Å) than those of Na–O (dipic). The remarkable difference in bond lengths can be attributed to steric congestion between the dipic anions, with respect to the relatively small radius of the Na^+ ion.

Figure 5 illustrates the uncommon coordination styles of the two dipic ligands in **2**. Dipic dianions act as multidentates and bridge manganese and sodium ions. One coordinates to three metal ions and provides five coordination sites, which binding manganese as a tridentate (O(1), O(3), N(1)), and connects two sodium ions via a μ_2-oxygen atom (O(2)) of a carboxylate group. The other dipic ligand is more complicated, and coordinates to five metal ions and with nine coordination sites. One of the two carboxylate groups is a tridentate to one Na^+ ion and chelates Mn^{2+} (O5 and O6); the other makes five bonds to three Na^+ ions and Mn^{2+} (O7 and O8). Among the four oxygen atoms, O5 and O6 chelate Na(2A); O7 and O8 chelate Na(2B) and O8 connects three Na^+ ions (Na (1A), Na (1B), Na (2B)) as a μ_3-oxygen atom. This complex bonding array is the first of its type to be observed.

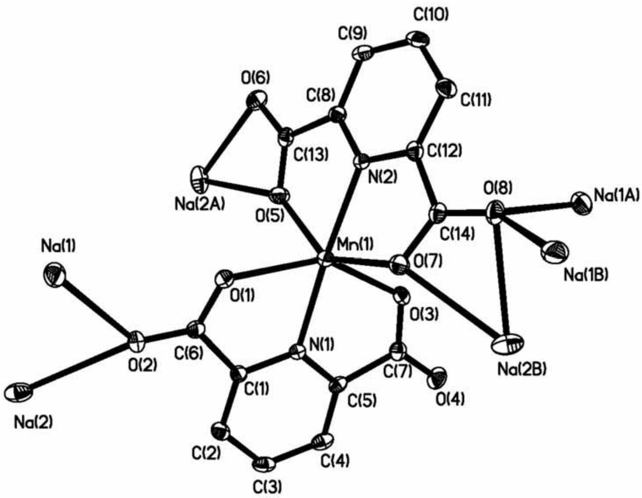

Figure 5. Coordination modes of the two dipic ligands.

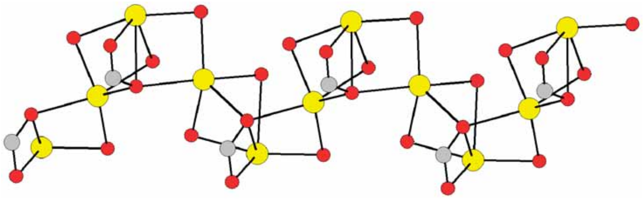

Figure 6. Simplified connectivity of sodium ions of **2**. The colour scheme is the same as in figure 2.

Sodium ions are connected through water oxygen atoms and carboxylate oxygen atoms to form a zigzag chain parallel to the *a* axis (figure 6). The manganese ions lie between the chains, connecting sodium ions through dipic anions. Figure 7 shows the complicated 3D network of **2**. Each Mn^{2+} ion is connected with six Na^+ ions and each Na^+ ion is linked to four Mn^{2+} ions through carboxylate groups (O–C–O or O). In this way, complex units are assembled into an infinite three-dimensional structure.

3.4. *Stability*

Both **1** and **2** are stable in air at ambient temperatures and are virtually insoluble in as water, alcohol, acetonitrile, chloroform, acetone and toluene, being consistent with their polymeric nature. Thermogravimetric analyses of both complexes were carried out under N_2. For **1** the first loss of 4.1% at 105°C corresponds to the loss of one water molecule pfu (Calcd 3.9%). Decomposition of dipic occurs in two steps at about 240 and 430°C. For **2** the first loss of 7.4% at 130°C corresponds to the loss of two water molecules pfu (Calcd 7.7%). Further weight loss due to ligand decomposition occurs at about 440°C.

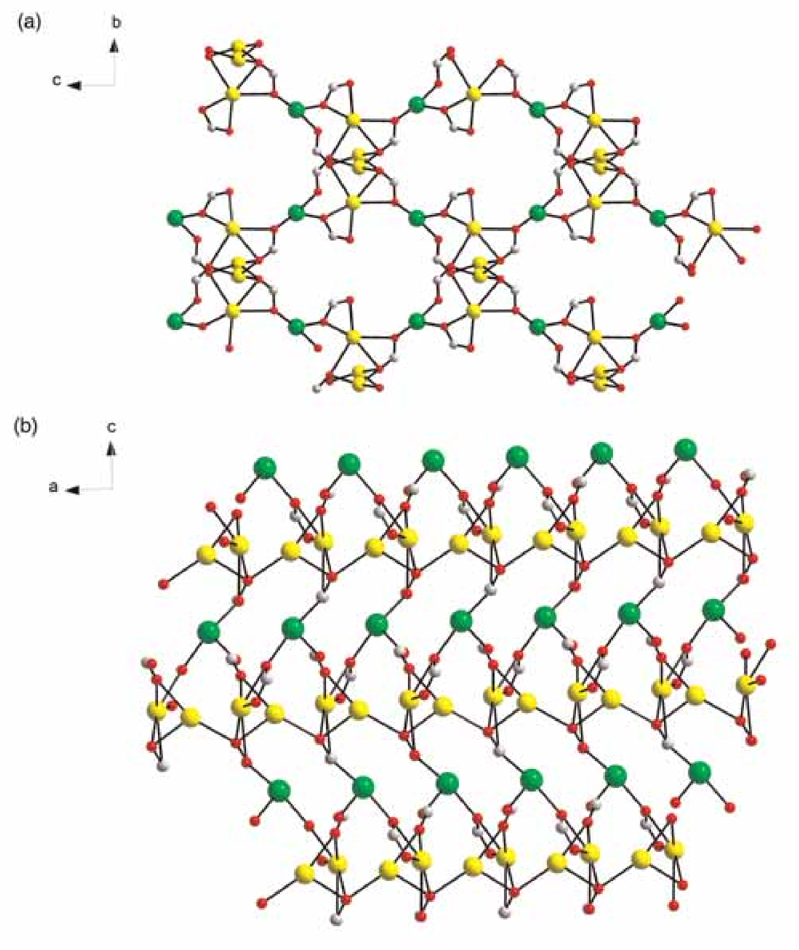

Figure 7. Packing views of **2**, (a) along the *a* axis; (b) along the *b* axis. The colour scheme is as for figure 2 with manganese as green spheres.

Supplementary data

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos 233843 and 264248. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk) or are available from the author Xiaoqing Wang.

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