

## Two two-dimensional Mn<sup>II</sup> and Na<sup>I</sup> coordination polymers constructed by the flexible benzene-1,4-dioxyacetate ligand

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Two new two-dimensional coordination polymers, poly[[[aqua(2,2'-bipyridine- $\kappa^2N,N'$ )manganese(II)]- $\mu_3$ -*p*-phenylenebis(oxyacetato)- $\kappa^3O:O':O''$ ] dihydrate], {[Mn(C<sub>10</sub>H<sub>8</sub>O<sub>6</sub>)(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)(H<sub>2</sub>O)]·2H<sub>2</sub>O}<sub>n</sub>, (I), and poly[[di- $\mu$ -aqua-bis[aqua-sodium(I)]]- $\mu_4$ -*p*-phenylenebis(oxyacetato)- $\kappa O:O',O'':O'''$ , - $O'''':O'''''$ ], [Na<sub>2</sub>(C<sub>10</sub>H<sub>8</sub>O<sub>6</sub>)(H<sub>2</sub>O)<sub>4</sub>]<sub>n</sub>, (II), have been synthesized and characterized by X-ray single-crystal diffraction. In (I), there are two 1,4-BDOA<sup>2-</sup> [*p*-phenylenebis(oxyacetate) or, more commonly, benzene-1,4-dioxyacetate] ligands, each lying about inversion centres, while in (II), there is one such ligand and it also has crystallographically imposed inversion symmetry. In (I), each Mn<sup>II</sup> atom displays an octahedral MnN<sub>2</sub>O<sub>4</sub> configuration, defined by three carboxyl O atoms of different 1,4-BDOA<sup>2-</sup> groups, two N atoms of one 2,2'-bipyridine ligand and one water molecule. In (II), each Na<sup>I</sup> atom is octahedrally coordinated by one ether O atom, two carboxyl O atoms of different 1,4-BDOA<sup>2-</sup> ligands and three water molecules. The metal ions in complexes (I) and (II) are bridged by 1,4-BDOA<sup>2-</sup> groups into two-dimensional layer structures. Furthermore, three-dimensional supramolecular networks are constructed *via* hydrogen bonds in (I) and (II), and by additional  $\pi$ - $\pi$  stacking interactions in (I).

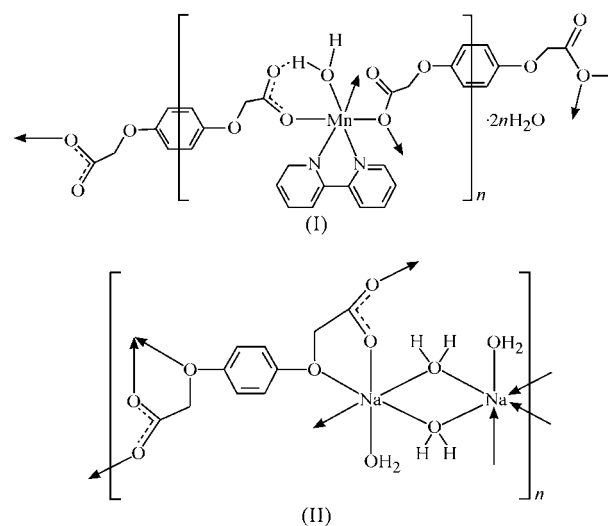
### Comment

Molecular self-assembly of coordination architectures has been a rapidly developing research area within supramolecular chemistry in recent years (Liu *et al.*, 2003). Ligand design is an important factor which greatly influences the structure of the coordination architecture and the functionality of the complex formed. To date, a number of metal-organic polymers with one-, two- and three-dimensional infinite frameworks have been generated (Lee *et al.*, 2003; Gutschke *et al.*, 2001), in which the more rigid aromatic polycarboxylic acids, such as

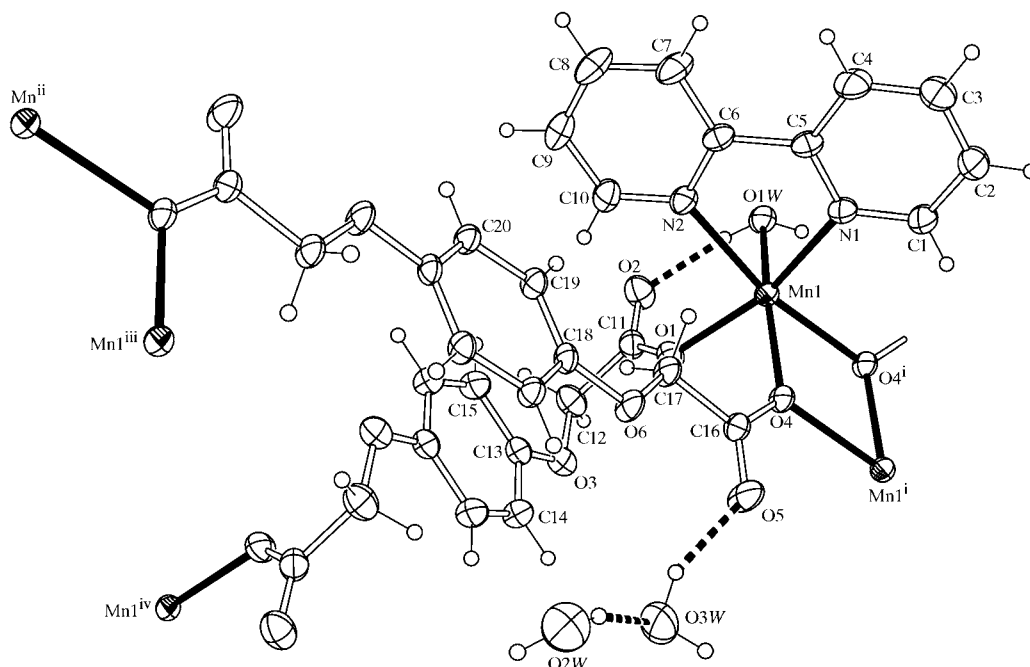
terephthalic acid or related species, are often chosen to fabricate the complexes (Gomez-Lor *et al.*, 2002; Bian *et al.*, 2003).

Previous studies by our group have shown that the flexible ligand benzene-1,4-dioxydiacetic acid (1,4-BDOAH<sub>2</sub>), an analogue of terephthalic acid, can exhibit versatile binding modes and forms a variety of topologies. In the case of the mononuclear [Mn(H<sub>2</sub>O)<sub>6</sub>](1,4-BDOA) complex, the 1,4-BDOA<sup>2-</sup> dianion functions as counter-ion (Liu, Gao, Huo, Zhao & Ng, 2004), while in the mononuclear [Co(1,4-BDOA)(2,2'-bipy)<sub>2</sub>(H<sub>2</sub>O)]·4H<sub>2</sub>O complex (2,2'-bipy is 2,2'-bipyridine), only one of the two oxyacetate groups of the 1,4-BDOA<sup>2-</sup> ligand, in a monodentate mode, is coordinated to the metal centre (Gao, Liu, Huo & Zhao, 2004).

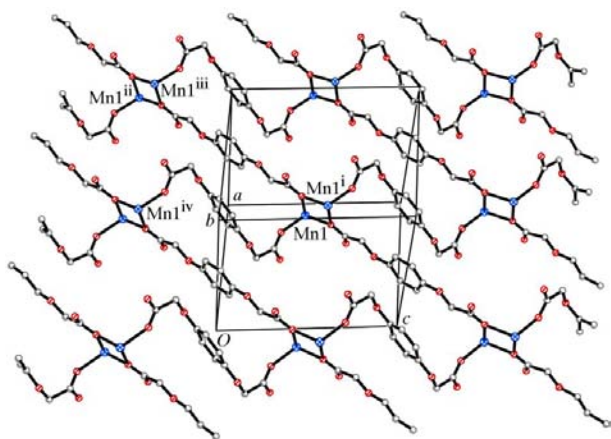
For one-dimensional coordination polymers, the 1,4-BDOA<sup>2-</sup> dianion acts in a great variety of coordination modes, such as bidentate (Gao *et al.*, 2004*c,d*; Liu, Gao, Huo, Zhao & Zhao, 2004), tridentate (Gao *et al.*, 2004*b,e*) or tetradentate (Gao, Liu, Huo, Zhao & Ng, 2004). In this paper, we report two novel two-dimensional coordination polymers, *viz.* {[Mn(1,4-BDOA)(2,2'-bipy)(H<sub>2</sub>O)]·2H<sub>2</sub>O}<sub>n</sub>, (I), and [Na<sub>2</sub>(1,4-BDOA)(H<sub>2</sub>O)<sub>4</sub>]<sub>n</sub>, (II), and describe their crystal structures.



As shown in Fig. 1, the asymmetric unit of (I) is composed of one Mn<sup>II</sup> atom, one 2,2'-bipy ligand, two halves of independent 1,4-BDOA<sup>2-</sup> groups lying about different inversion centres, one coordinated water molecule and two solvate water molecules. The carboxylate groups bind to each Mn<sup>II</sup> atom in a monodentate fashion. Each Mn<sup>II</sup> centre is coordinated by three carboxyl O atoms from different 1,4-BDOA<sup>2-</sup> groups, two N atoms from one 2,2'-bipy ligand and one water molecule, resulting in a distorted octahedral environment. The Mn<sup>II</sup> atom does not deviate significantly from the equatorial plane of atoms O1/O4<sup>i</sup>/N1/N2 [displacement = 0.01 (2) Å; symmetry code: (i) 1 - x, 1 - y, 1 - z]. The Mn1—O1 distance (Table 1) is slightly shorter than both Mn1—O4 and Mn1—O4<sup>i</sup>. The 2,2'-bipy ligand connects the Mn<sup>II</sup> atom to form a five-membered chelate ring, with a mean Mn—N distance of 2.28 (3) Å and an N1—Mn1—N2 bond angle of 72.14 (5)°.


**Figure 1**

A view of complex (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are indicated by dashed lines. [Symmetry codes: (i)  $1 - x, 1 - y, 1 - z$ ; (ii)  $1 + x, y, z - 1$ ; (iii)  $2 - x, 1 - y, -z$ ; (iv)  $1 - x, 1 - y, -z$ .]


**Figure 2**

The two-dimensional layer structure of (I), with the 2,2'-bipy ligand and water molecules omitted for clarity. Symmetry codes are as in Fig. 1.

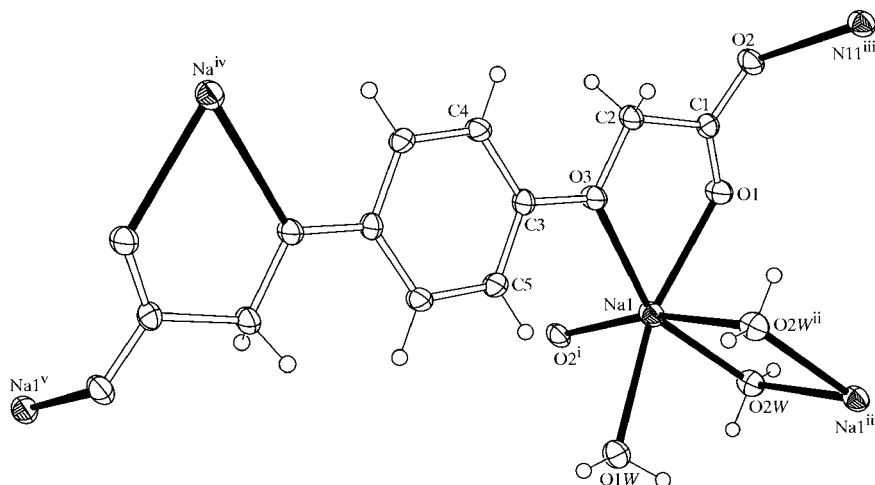
It should be noted that the two C—O bond distances of the carboxyl group (O1—C11—O2) are almost equivalent, agreeing with its delocalized state, whereas the O4—C16 distance is longer than the O5—C16 distance, in accord with the formal double-bond character of the O5—C16 bond. This is also reflected by the fact that the two carboxyl groups are involved in coordination to Mn, exhibiting a monodentate-linked mode *via* atom O1 and a bidentate-bridged mode *via* atom O4. The bidentate-bridged oxyacetate group and aromatic ring are almost coplanar, with the C18—O6—C17—C16 torsion angle being  $175.12(13)^\circ$ . In contrast, the monodentate-linked oxyacetate group is twisted out the aromatic ring plane, with the C13—O3—C2—C1 torsion angle being

$80.0(2)^\circ$ . The 2,2'-bipy ligand is nearly perpendicular to the two phenyl rings, with dihedral angles of  $88.6(2)$  and  $89.8(2)^\circ$ .

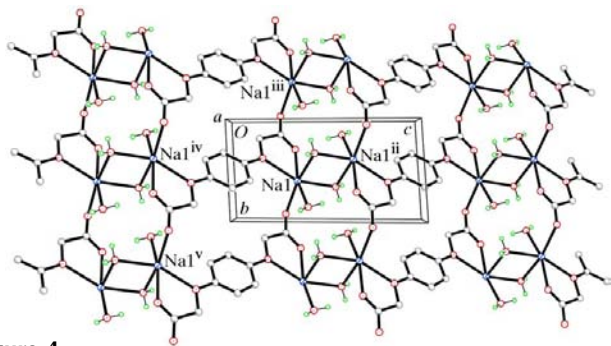
Fig. 2 shows the two-dimensional layer structure of (I). Two  $\text{MnN}_2\text{O}_4$  octahedral units are linked by carboxyl atoms O4 and O4<sup>i</sup> to form a binuclear unit [ $\text{Mn1}\cdots\text{Mn1}^i = 3.588(2) \text{ \AA}$ ]. All the binuclear units are bridged by one 1,4-BDOA<sup>2-</sup> group in tetradentate mode, to produce a one-dimensional chain, with  $\text{Mn1}\cdots\text{Mn1}^{ii} = 14.537(2)$ ,  $\text{Mn1}\cdots\text{Mn1}^{iii} = 13.428(2)$  and  $\text{Mn1}^i\cdots\text{Mn1}^{ii} = 16.373(2) \text{ \AA}$  [symmetry codes: (ii)  $1 + x, y, z - 1$ ; (iii)  $2 - x, 1 - y, -z$ ]. These infinite chains are further connected together by another 1,4-BDOA<sup>2-</sup> group in a bidentate mode [ $\text{Mn1}\cdots\text{Mn1}^{iv} = 11.401(2) \text{ \AA}$ ; symmetry code: (iv)  $1 - x, 1 - y, -z$ ], generating a two-dimensional architecture running in the crystallographic *bc* plane. In addition, the chains are connected through extensive hydrogen bonds involving the water molecules and 1,4-BDOA groups, with O $\cdots$ O distances in the range  $2.655(2)$ – $2.822(3) \text{ \AA}$  (Table 2).

There are partial face-to-face  $\pi$ – $\pi$  stacking interactions between adjacent 2,2'-bipy ligands. The centroid–centroid separation between ring N1/C1–C5 and ring N2/C6–C10 at  $(2 - x, -y, 1 - z)$  is  $3.898(2) \text{ \AA}$ , and the shortest C $\cdots$ C separation is  $\text{C2}\cdots\text{C8}(2 - x, -y, 1 - z)$  of  $3.593(3) \text{ \AA}$ . With the help of such interactions, the polymeric chains are assembled to form a three-dimensional supramolecular network.

As illustrated in Fig. 3, the asymmetric unit of (II) consists of one  $\text{Na}^+$  atom, half of a 1,4-BDOA<sup>2-</sup> group lying about an inversion centre and two coordinated water molecules. The unique ether O atom of the 1,4-BDOA<sup>2-</sup> group coordinates to the  $\text{Na}^+$  centre. The coordination sphere of the  $\text{Na}^+$  atom has distorted octahedral geometry, the basal plane consisting of

**Figure 3**

A view of complex (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i)  $x, 1 - y, 1 - z$ ; (ii)  $1 - x, 1 - y, 1 - z$ ; (iii)  $x, y - 1, z$ ; (iv)  $2 - x, 1 - y, -z$ ; (v)  $2 - x, 2 - y, z$ .]

**Figure 4**

The two-dimensional layer structure of (II). Symmetry codes are as in Fig. 3.

carboxyl atom O1, ether atom O3 of the 1,4-BDOA<sup>2-</sup> group and two water molecules (O1W and O2W) [r.m.s. deviation = 0.04 (1) Å; deviation of Na1 from the basal plane = -0.34 (2) Å], while the axial coordination sites are occupied by carboxyl atom O2<sup>ii</sup> and water molecule O2W<sup>i</sup> (see Table 3 for symmetry codes). The Na1—O1W bond distance (terminal water) (Table 3) is somewhat longer than Na1—O2W and Na—O2W<sup>i</sup> (bridging waters) and lies within the range of the corresponding bond distances [2.365 (2)–2.485 (2) Å] in the complex [Na(1,3-BDOA)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>][Cr(H<sub>2</sub>O)<sub>6</sub>].5H<sub>2</sub>O, (III) (Gao, Liu, Huo, Zhao & Zhao, 2004a).

The Na—O<sub>ether</sub> and Na—O<sub>carboxyl</sub> bond distances in (II) are shorter than the corresponding bond distances in complex (III) [Na—O<sub>ether</sub> 2.966 (2) Å, and Na—O<sub>carboxyl</sub> 2.381 (2) and 2.635 (2) Å]. In (III), each Na atom displays a distorted trigonal prism geometry, involving two carboxyl O atoms and one ether O atom of different oxyacetate groups, and three water molecules. These differences are probably due to steric effects from the unusual coordination mode for the 1,4-BDOA<sup>2-</sup> group in (II) compared with the 1,3-BDOA<sup>2-</sup> group in (III).

In (II), the oxyacetate group combines with the Na<sup>I</sup> centre through ether atom O3 and carboxyl atom O1 to give one five-

membered chelate plane (O1—C1—C2—O3—Na); the r.m.s. deviation for the five atoms is 0.01 (2) Å. The C—O bond distances of the unique carboxyl group do not differ, in accord with the electron delocalization. The oxyacetate group and the benzene ring are essentially coplanar, with a C3—O3—C2—C1 torsion angle of 175.08 (11)°.

The 1,4-BDOA<sup>2-</sup> group in (II) serves as a rare hexadentate ligand, constructing a two-dimensional coordination polymer (Fig. 4). Two adjacent octahedral units are linked together by two H<sub>2</sub>O bridges to form a four-membered ring with an Na<sub>2</sub>O<sub>2</sub> core. The Na1···Na1<sup>iii</sup> separation is 3.582 (2) Å [symmetry code: (ii)  $1 - x, 1 - y, 1 - z$ ]. Adjacent Na<sub>2</sub>O<sub>2</sub> binuclear motifs are further joined by the oxyacetate groups of 1,4-BDOA<sup>2-</sup> ligands through carboxyl atom O1 and ether atom O3, to produce a one-dimensional chain along the *c* axis, with an Na1···Na1<sup>iv</sup> separation of 9.233 (2) Å [symmetry code: (iv)  $2 - x, 1 - y, -z$ ]; this is significantly longer than the corresponding Na···Na distance of 8.006 (3) Å in the three-dimensional Na-terephthalate polymer [Na<sub>2</sub>(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>)] (Kaduk, 2000). These chains are connected by the other carboxyl O atoms of the 1,4-BDOA ligands [Na1···Na1<sup>iii</sup> = 5.914 (2) Å and Na1···Na1<sup>v</sup> = 10.301 (2) Å; symmetry codes: (iii)  $x, y - 1, z$ ; (v)  $2 - x, 2 - y, z$ ], generating a two-dimensional layer architecture in the crystallographic *bc* plane. These layers are stabilized by intermolecular hydrogen bonds, which are formed between the water molecules and carboxyl O atoms, with O···O distances in the range 2.757 (2)–2.938 (2) Å (Table 4), leading to the formation of a three-dimensional supramolecular network.

It is the conformational flexibility of the 1,4-BDOA<sup>2-</sup> ligand, with bidentate and tridentate bridging modes in complex (I) and a hexadentate bridging mode in complex (II), which leads to the formation of these two novel two-dimensional layer complexes, with octahedral geometries for the metal ions as well as different arrangements of the whole structures.

Experimental

Benzene-1,4-dioxyacetic acid was prepared following the method described for the synthesis of benzene-1,2-dioxyacetic acid by Mirci (1990). Complex (I) was synthesized by the addition of MnCl<sub>2</sub>·6H<sub>2</sub>O (4.68 g, 20 mmol) and 2,2'-bipy (2.12 g, 20 mmol) to a hot aqueous solution of 1,4-BDOAH<sub>2</sub> (4.52 g, 20 mmol). The solution was allowed to evaporate at room temperature and yellow crystals of (I) were obtained after about 7 d. Analysis calculated for C<sub>20</sub>H<sub>22</sub>MnN<sub>2</sub>O<sub>9</sub>: C 49.09, H 4.53, N 5.72%; found: C 49.15, H 4.48, N 5.69%. Complex (II) was prepared by the addition of stoichiometric amounts of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (4.96 g, 10 mmol), imidazole (0.95 g, 10 mmol) and NaOH (0.80 g, 20 mmol) to a hot aqueous solution of 1,4-BDOAH<sub>2</sub> (2.26 g, 10 mmol), with subsequent filtration. Colourless crystals of (II) were obtained at room temperature over several days. Analysis calculated for C<sub>10</sub>H<sub>16</sub>Na<sub>2</sub>O<sub>10</sub>: C 35.10, H 4.71%; found: C 35.29, H 4.63%.

Compound (I)

Crystal data

[Mn(C<sub>10</sub>H<sub>8</sub>O<sub>6</sub>)(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)(H<sub>2</sub>O)]·2H<sub>2</sub>O  
*M<sub>r</sub>* = 489.34  
 Triclinic, *P* $\bar{1}$   
*a* = 9.3142 (19) Å  
*b* = 10.315 (2) Å  
*c* = 12.169 (2) Å  
 $\alpha$  = 87.87 (3)°  
 $\beta$  = 84.04 (3)°  
 $\gamma$  = 68.68 (3)°  
*V* = 1083.3 (4) Å<sup>3</sup>

*Z* = 2  
*D<sub>x</sub>* = 1.500 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 5624 reflections  
 $\theta$  = 3.0–27.5°  
 $\mu$  = 0.66 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Prism, pale yellow  
 0.41 × 0.32 × 0.21 mm

Data collection

Rigaku R-Axis RAPID diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)  
*T<sub>min</sub>* = 0.773, *T<sub>max</sub>* = 0.873  
 10 496 measured reflections

4928 independent reflections  
 4461 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.014  
 $\theta_{max}$  = 27.5°  
*h* = -12 → 12  
*k* = -12 → 13  
*l* = -15 → 15

Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.036  
*wR* (*F*<sup>2</sup>) = 0.094  
*S* = 1.06  
 4928 reflections  
 307 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 0.2938P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.001$   
 $\Delta\rho_{max} = 0.41 \text{ e \AA}^{-3}$   
 $\Delta\rho_{min} = -0.17 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °) for (I).

Mn1—N1	2.2511 (15)	Mn1—O1W	2.2124 (14)
Mn1—N2	2.3031 (17)	O1—C11	1.255 (2)
Mn1—O1	2.1298 (13)	O2—C11	1.247 (2)
Mn1—O4	2.2241 (12)	O4—C16	1.2760 (18)
Mn1—O4 <sup>i</sup>	2.2794 (14)	O5—C16	1.227 (2)
N1—Mn1—N2	72.14 (5)	O4—Mn1—N2	111.09 (5)
N1—Mn1—O4 <sup>i</sup>	97.29 (5)	O4 <sup>i</sup> —Mn1—N2	168.19 (5)
O1—Mn1—N1	161.61 (5)	O4—Mn1—O4 <sup>i</sup>	74.38 (5)
O1—Mn1—N2	90.73 (5)	O1W—Mn1—N1	95.06 (6)
O1—Mn1—O4	84.79 (5)	O1W—Mn1—N2	83.69 (5)
O1—Mn1—O4 <sup>i</sup>	100.33 (5)	O1W—Mn1—O4	164.16 (4)
O1—Mn1—O1W	89.49 (6)	O1W—Mn1—O4 <sup>i</sup>	92.21 (5)
O4—Mn1—N1	94.99 (6)		

Symmetry code: (i) 1 - *x*, 1 - *y*, 1 - *z*.

Table 2

Hydrogen-bonding geometry (Å, °) for (I).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1W—H1W1...O5 <sup>i</sup>	0.84 (3)	1.87 (3)	2.655 (2)	153 (2)
O1W—H1W2...O2	0.85 (3)	1.87 (3)	2.695 (2)	164 (2)
O3W—H3W1...O2 <sup>ii</sup>	0.86 (3)	1.90 (3)	2.763 (3)	174 (4)
O3W—H3W2...O5	0.86 (3)	1.89 (2)	2.695 (2)	154 (4)
O2W—H2W1...O3W	0.88 (3)	1.93 (3)	2.795 (4)	165 (4)
O2W—H2W2...O3W <sup>iii</sup>	0.88 (3)	1.96 (3)	2.822 (3)	171 (4)

Symmetry codes: (i) 1 - *x*, 1 - *y*, 1 - *z*; (ii) *x*, 1 + *y*, *z*; (iii) 1 - *x*, 2 - *y*, -*z*.

Compound (II)

Crystal data

[Na<sub>2</sub>(C<sub>10</sub>H<sub>8</sub>O<sub>6</sub>)(H<sub>2</sub>O)<sub>4</sub>]  
*M<sub>r</sub>* = 342.21  
 Triclinic, *P* $\bar{1}$   
*a* = 5.3754 (11) Å  
*b* = 5.9136 (12) Å  
*c* = 11.236 (2) Å  
 $\alpha$  = 85.83 (3)°  
 $\beta$  = 82.01 (3)°  
 $\gamma$  = 83.54 (3)°  
*V* = 350.87 (12) Å<sup>3</sup>

*Z* = 1  
*D<sub>x</sub>* = 1.620 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 2648 reflections  
 $\theta$  = 3.9–27.5°  
 $\mu$  = 0.19 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Prism, colourless  
 0.38 × 0.24 × 0.17 mm

Data collection

Rigaku R-Axis RAPID diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)  
*T<sub>min</sub>* = 0.930, *T<sub>max</sub>* = 0.968  
 3380 measured reflections

1588 independent reflections  
 1415 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.014  
 $\theta_{max}$  = 27.5°  
*h* = -6 → 6  
*k* = -7 → 7  
*l* = -14 → 14

Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.037  
*wR* (*F*<sup>2</sup>) = 0.099  
*S* = 1.06  
 1588 reflections  
 112 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0604P)^2 + 0.0805P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.41 \text{ e \AA}^{-3}$   
 $\Delta\rho_{min} = -0.17 \text{ e \AA}^{-3}$

Table 3

Selected geometric parameters (Å, °) for (II).

Na1—Na1 <sup>i</sup>	3.582 (2)	Na1—O2W <sup>i</sup>	2.423 (2)
Na1—O1	2.343 (2)	O1—C1	1.256 (2)
Na1—O2 <sup>ii</sup>	2.413 (2)	O2—C1	1.253 (2)
Na1—O3	2.483 (2)	O3—C2	1.423 (2)
Na1—O1W	2.459 (2)	O3—C3	1.383 (2)
Na1—O2W	2.362 (2)		
O1—Na1—Na1 <sup>i</sup>	85.21 (4)	O1W—Na1—Na1 <sup>i</sup>	78.84 (4)
O1—Na1—O2 <sup>ii</sup>	110.55 (4)	O1W—Na1—O3	114.08 (5)
O1—Na1—O3	66.75 (4)	O2W <sup>i</sup> —Na1—Na1 <sup>i</sup>	40.87 (3)
O1—Na1—O1W	161.53 (5)	O2W—Na1—Na1 <sup>i</sup>	42.18 (3)
O1—Na1—O2W	91.18 (5)	O2W—Na1—O2 <sup>ii</sup>	91.69 (5)
O1—Na1—O2W <sup>i</sup>	81.75 (4)	O2W—Na1—O3	155.35 (4)
O2 <sup>ii</sup> —Na1—Na1 <sup>i</sup>	132.69 (4)	O2W <sup>i</sup> —Na1—O3	83.00 (5)
O2 <sup>vii</sup> —Na1—O3	105.90 (5)	O2W—Na1—O1W	83.28 (5)
O2 <sup>ii</sup> —Na1—O1W	87.29 (4)	O2W <sup>i</sup> —Na1—O1W	80.10 (4)
O2 <sup>ii</sup> —Na1—O2W <sup>i</sup>	166.81 (4)	O2W—Na1—O2W <sup>i</sup>	83.05 (5)
O3—Na1—Na1 <sup>i</sup>	121.12 (4)		

Symmetry codes: (i) 1 - *x*, 1 - *y*, 1 - *z*; (ii) *x*, 1 + *y*, *z*.

C-bound H atoms were placed in calculated positions, with C—H = 0.93 or 0.97 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C), and were refined in the

**Table 4**

Hydrogen-bonding geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1W-H1W1\cdots O1^i$	0.851 (12)	2.095 (12)	2.938 (2)	170 (2)
$O1W-H1W2\cdots O2^{ii}$	0.849 (13)	1.908 (13)	2.757 (2)	179 (2)
$O2W-H2W1\cdots O1W^{iii}$	0.853 (13)	2.072 (12)	2.876 (2)	157 (2)
$O2W-H2W2\cdots O1^{iv}$	0.860 (13)	1.936 (13)	2.778 (2)	166 (2)

Symmetry codes: (i)  $1-x, 1-y, 1-z$ ; (ii)  $1+x, 1+y, z$ ; (iii)  $1-x, 2-y, 1-z$ ; (iv)  $-x, 1-y, 1-z$ .

riding-model approximation. Water H atoms were located in a difference map and refined with O—H distance restraints of 0.85 (1) Å and with  $U_{iso}(H) = 1.5U_{eq}(O)$ .

For both compounds, data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1790). Services for accessing these data are described at the back of the journal.

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