Magnetic properties of two double-layer structures built from hydroxynaphthoic acids and manganese

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Double-layer structures consisting of alternating polar and non-polar layers have been prepared using Mn^{2+} ions and o-hydroxynaphthoic acids. The polar layers contain the Mn^{2+} ions, carboxylate groups, hydroxy groups and water molecules. The non-polar layers are built up from the naphthalene moieties. In catena-poly[[diaquamanganese(II)]bis(μ-3-hydroxy-2-naphthoato-$\kappa^2 O$:O')] (also called manganese 3-hydroxy-2-naphthoate dihydrate), [Mn(C₁₁H₇O₃)₂(H₂O)₂]ₙ, (I), the Mn^{2+} ions are connected by carboxylate groups to form two-dimensional networks. This compound shows distinct antiferromagnetic interactions and long-range ordering at low temperature. In contrast, tetraaquabis(1-hydroxy-2-naphthoato-κO)manganese(II), [Mn(C₁₁H₇O₃)₂(H₂O)₄], (II), which lacks a close linkage between the Mn^{2+} ions, reveals purely paramagnetic behaviour. In (II), the Mn^{2+} ion lies on an inversion centre.

Comment

Low-dimensional spin systems are a topic of current research because of their unusual magnetic properties. In the course of searching for molecule-based new materials, we have designed double-layer structures consisting of alternating polar and non-polar layers (Fig. 1). Each polar layer contains a two-dimensional network of metal ions, carboxylate groups and water molecules, and these networks are separated by non-polar layers of naphthalene fragments of considerable thickness. The structures are built from Mn^{2+} ions and 3-hydroxy-2-naphthoate or 1-hydroxy-2-naphthoate anions. 3-Hydroxy-2-naphthoic acid is also known as β-oxynaphthoic acid (BONA) and is used industrially for the synthesis of red azo pigments (Herbst & Hunger, 2004).

Transition metal complexes with hydroxynaphthoates as ligands have rarely been synthesized or crystallized, although the starting materials are readily available. Crystal structures have not been reported to date, except for some lanthanoid complexes (Ohki et al., 1986; Ohki, Suzuki & Ouchi, 1987; Ohki, Suzuki, Shimoi & Ouchi, 1987). Reasons include problems in growing single crystals as well as synthetic difficulties: hydroxynaphthoic acids are insoluble in water and acids, while Mn^{2+} salts are often insoluble in alkaline media and organic solvents. Therefore, most synthetic attempts result in mixtures of starting materials (cf. Schmidt et al., 2002). Furthermore, the synthesized metal complexes reveal very low solubilities in most media, which renders the growth of single crystals suitable for X-ray analysis difficult. We finally succeeded in growing single crystals of the title compounds, (I)
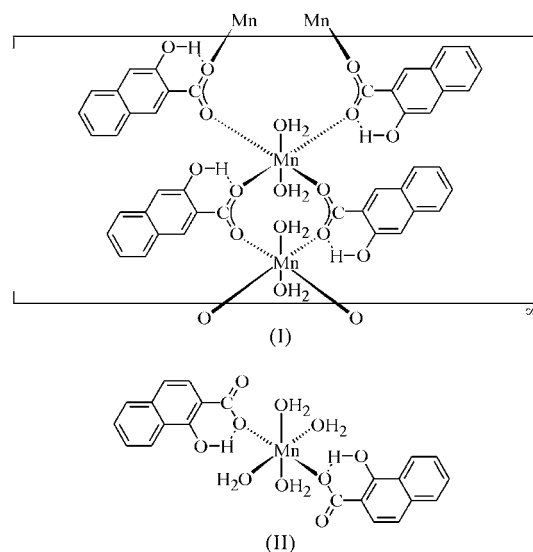
and (II), by slow reaction of a mixture of $Mn(OH)_2$ suspensions and hydroxynaphthoic acid suspensions in water. The crystals form plate-like species, as expected for layer structures with strong hydrogen bonds and Coulomb interactions within the layers and weak van der Waals interactions between the layers. The crystal structures of (I) and (II) were determined by single-crystal X-ray diffraction. As intended, both compounds form double-layer structures. The crystal of (I) was found to be a non-merohedral twin.

In both compounds, the Mn^{2+} ions are coordinated octahedrally by six O atoms. In (I), the Mn^{2+} ion is coordinated by four carboxylate groups of four different molecules of
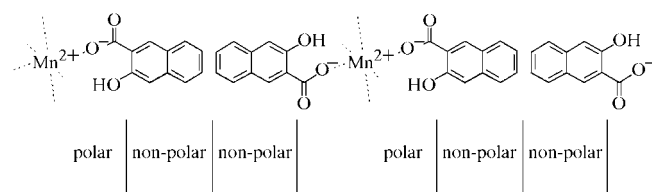

Figure 1
A schematic view of the designed structures consisting of alternating polar and non-polar layers.

3-hydroxy-2-naphthoate in a square-planar type arrangement. The remaining two axial positions of the octahedra are occupied by water molecules (Fig. 2). Each carboxylate group connects two Mn^{2+} ions. The closest $Mn\cdots Mn$ distances are 4.392 (1) and 5.135 (1) Å. The shorter distance is bridged simultaneously by two carboxylate groups and the longer distance by only one carboxylate group. Accordingly, the structure contains two crystallographically independent 3-hydroxy-2-naphthoate moieties. The Mn^{2+} ions are situated on a general position. The closest $Mn\cdots Mn$ distances between Mn^{2+} ions of different layers is as large as 17.262 (2) Å.

In compound (II), the Mn^{2+} ion is coordinated by only two molecules of 1-hydroxy-2-naphthoate in the axial positions and four water molecules arranged in the equatorial square plane of the coordination octahedron (Fig. 3). The Mn^{2+} ions are positioned on a crystallographic inversion centre. The closest $Mn\cdots Mn$ distance is 5.2121 (3) Å.

The Mn—O distances are between 2.109 (6) and 2.246 (6) Å for both compounds (Tables 1 and 3). All O—Mn—O angles are in the range 83.5 (2)–98.8 (2)° for O atoms in *cis* positions and in the range 167.4 (3)–180° for O atoms in *trans* positions. In both compounds, the hydroxy groups do not participate in the octahedral coordination of the Mn^{2+} ions; the OH^- groups only form intramolecular hydrogen bonds to neighbouring carboxylate groups.

Despite this similarity, the structures differ in various aspects. The crystal structure of (I) contains a parallel arrangement of naphthalene moieties within the non-polar layer (Fig. 4); this packing motif is also known for aromatic compounds, *e.g.* for hexamethylbenzene (Lonsdale, 1929). In contrast, in (II), the naphthalene moieties form a herring-bone arrangement (Fig. 5), as in naphthalene itself (Bragg, 1921) and many other aromatic compounds. Furthermore, both compounds show different types of connection pattern for the Mn^{2+} ions. In compound (I), neighbouring Mn^{2+} ions are connected by carboxylate groups, which provide a magnetic exchange path *via* Mn—O—C—O—Mn (Fig. 6). In fact, susceptibility measurements on this material revealed a significant antiferromagnetic interaction between the Mn^{2+} ions. For high temperatures in the range 50 K $\leq T \leq$ 300 K, the susceptibility follows a Curie–Weiss-like temperature dependence, $\chi(T) = C/(T+\theta)$, corresponding to Mn^{2+} ($S = \frac{5}{2}$) ions with an average antiferromagnetic interaction $\theta_{AF} = (12\pm0.2)$ K (Fig. 7). With decreasing temperature, the susceptibility shows a distinct maximum at $T_{max} = 8$ K. Such a temperature dependence is known for Mn^{2+} systems with quasi-one- or two-dimensional antiferromagnetic interactions (Smith & Friedberg, 1968). We assigned the kink in $\chi(T)$ at $T_N = (3\pm0.2)$ K to the onset of three-dimensional antiferromagnetic ordering. Since low-range magnetic order at a finite temperature is not expected for Heisenberg interactions in dimensions $d < 3$ (Mermin & Wagner, 1966), this observation implies a significant magnetic coupling between the layers, probably mediated *via* the naphthalene fragments.

In contrast, compound (II) does not show such an exchange path. The two-dimensional network is built by isolated Mn–
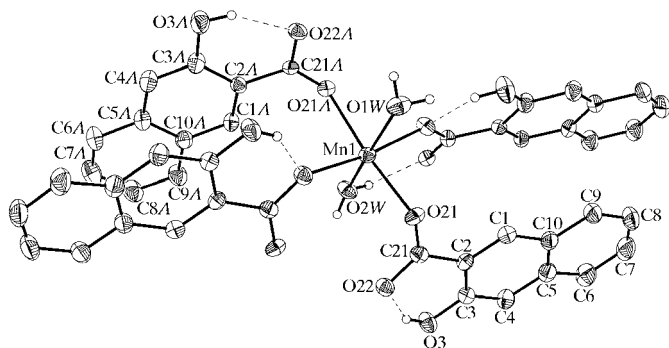

Figure 2
The coordination of the Mn^{2+} ions in (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by spheres of arbitrary size. The H atoms of the naphthalene moieties have been omitted for clarity. Hydrogen bonds are indicated by dashed lines.
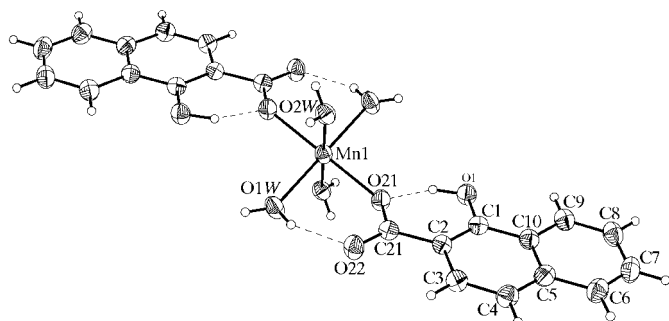

Figure 3
The coordination of the Mn^{2+} ions in (II). Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by spheres of arbitrary size. Hydrogen bonds are indicated by dashed lines.
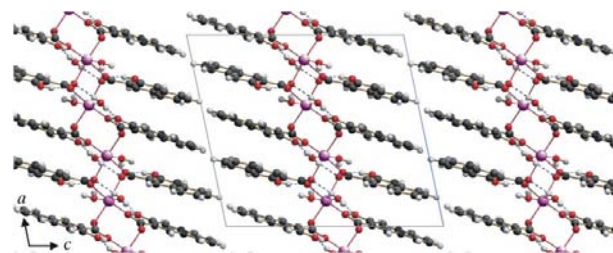

Figure 4
The structure of (I), viewed along the [010] direction. Hydrogen bonds are indicated by dashed lines.
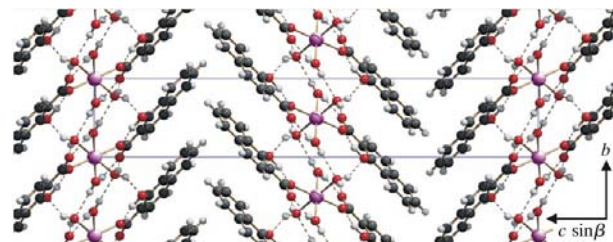

Figure 5
The structure of (II), viewed along the [100] direction. Hydrogen bonds are indicated by dashed lines.

bis-naphthoate moieties which are connected by water molecules. This leads to an arrangement which is not expected to mediate magnetic interaction between the Mn^{2+} ions. Indeed, the compound shows paramagnetic behaviour. The temperature dependence of the magnetic susceptibility was found to follow a simple Curie law, with a Curie constant corresponding to uncoupled $S = \frac{5}{2}$ spins and an isotropic g factor of 2. This observation of magnetically isolated paramagnetic centres is consistent with the crystal structure, where the Mn^{2+} ions in their $^6S_{\frac{5}{2}}$ ground-state configuration lack any obvious magnetic

exchange path to neighbouring Mn^{2+} ions. As an upper limit for a possible magnetic Mn^{2+}–Mn^{2+} interaction, we estimate an antiferromagnetic Weiss temperature of $\theta_{AF} = (0.7 \pm 0.5)$ K.

Experimental

For the preparation of compound (I), a suspension of $Mn(OH)_2$ (0.25 g) in H_2O (65 ml) was added to a suspension of 3-hydroxy-2-naphthoic acid (BONA; 1.50 g) in water (100 ml). The mixture was heated at 313 K for 6 weeks. The crystals grew as thin brown plates with sizes up to 1 mm. They were separated by decantation and dried in air at room temperature (yield ca 90%). For the preparation of compound (II), a suspension of $Mn(OH)_2$ (0.35 g) in H_2O (60 ml) was added to a suspension of 1-hydroxy-2-naphthoic acid (1.75 g, 1,2-HNA) in water (100 ml). The mixture was heated at 313 K for 6 weeks. Red–brown crystals of sizes up to 1 mm were obtained after decantation and dried in air at room temperature (yield ca 90%). In both cases, X-ray powder investigation did not give any hint of additional compounds or phases, or of remains of the starting materials. Variable-temperature magnetic susceptibility measurements in the temperature range 2–300 K and magnetic fields of 0.5–2 T were carried out on single-crystal samples of (I) ($m = 0.65$ mg) and (II) ($m = 2.35$ mg) using a Quantum Design SQUID magnetometer. These measurements were complemented by isothermal magnetization runs at temperatures of 2–200 K and fields up to 5 T. The data were corrected for the contribution of the sample holder and for the diamagnetic core contribution.

Compound (I)

Crystal data

$[Mn(C_{11}H_7O_3)_2(H_2O)_2]$	$D_x = 1.602$ Mg m^{-3}
$M_r = 465.30$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 20695
$a = 17.2616\,(17)$ Å	reflections
$b = 7.3476\,(5)$ Å	$\theta = 2.5$–$27.3°$
$c = 15.5360\,(15)$ Å	$\mu = 0.74$ mm^{-1}
$\beta = 101.815\,(8)°$	$T = 173\,(2)$ K
$V = 1928.7\,(3)$ Å^3	Plate, light brown
$Z = 4$	$0.42 \times 0.32 \times 0.13$ mm

Data collection

Stoe IPDS-II two-circle	4535 independent reflections
diffractometer	3911 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.083$
Absorption correction: multi-scan	$\theta_{max} = 28.0°$
(*MULABS*; Spek, 1990;	$h = -22 \rightarrow 22$
Blessing, 1995)	$k = -9 \rightarrow 9$
$T_{min} = 0.748$, $T_{max} = 0.911$	$l = -20 \rightarrow 20$
17865 measured reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0999P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.087$	$+ 24.9072P]$
$wR(F^2) = 0.316$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.21$	$(\Delta/\sigma)_{max} < 0.001$
4535 reflections	$\Delta\rho_{max} = 1.08$ e Å^{-3}
281 parameters	$\Delta\rho_{min} = -1.27$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å) for (I).

Mn1—O22^i	2.109 (6)	Mn1—O22A^{ii}	2.170 (6)
Mn1—O2W	2.159 (6)	Mn1—O1W	2.198 (7)
Mn1—O21	2.163 (6)	Mn1—O21A	2.246 (6)

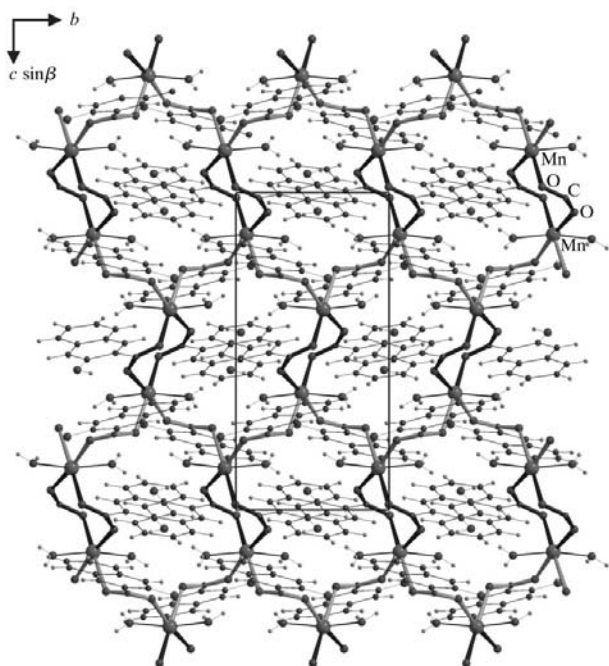Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$.

Figure 6
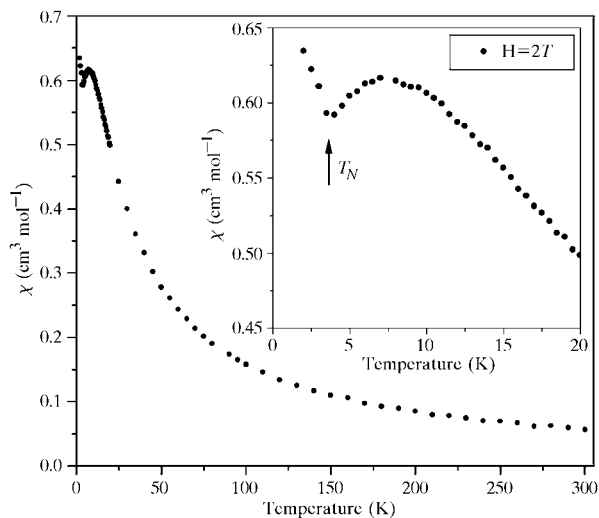The magnetic exchange path in (I), viewed along the [100] direction.

Figure 7
The magnetic susceptibility of (I). The inset shows the low-temperature region. The arrow indicates the onset of long-range antiferromagnetic order (see *Comment*).

Table 2
Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3$\cdots$O22	0.84	1.78	2.533 (9)	148
O3A—H3$A\cdots$O22A	0.84	1.84	2.582 (9)	146
O1W—H1$WA\cdots$O21A^{iii}	0.84	2.01	2.846 (9)	180
O1W—H1$WB\cdots$O3A^{ii}	0.84	2.56	3.351 (10)	157
O2W—H2$WA\cdots$O21A^{ii}	0.84	1.99	2.834 (9)	180
O2W—H2$WB\cdots$O3$^{\text{iv}}$	0.84	1.91	2.751 (9)	180

Symmetry codes: (ii) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x+1, -y, -z+1$.

Compound (II)

Crystal data

[Mn(C$_{11}$H$_7$O$_3$)$_2$(H$_2$O)$_4$]
$M_r = 501.34$
Monoclinic, $P2_1/n$
$a = 6.8188$ (5) Å
$b = 5.2121$ (3) Å
$c = 29.639$ (3) Å
$\beta = 94.917$ (7)°
$V = 1049.51$ (13) Å^3
$Z = 2$

$D_x = 1.586$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25353 reflections
$\theta = 2.6–28.2°$
$\mu = 0.69$ mm^{-1}
$T = 173$ (2) K
Plate, light brown
$0.26 \times 0.22 \times 0.13$ mm

Data collection

Stoe IPDS-II two-circle diffractometer
ω scans
Absorption correction: multi-scan (*MULABS*; Spek, 1990; Blessing, 1995)
$T_{\min} = 0.841$, $T_{\max} = 0.916$
22886 measured reflections

2576 independent reflections
2158 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.062$
$\theta_{\max} = 28.2°$
$h = -9 \rightarrow 9$
$k = -6 \rightarrow 6$
$l = -39 \rightarrow 39$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.113$
$S = 1.11$
2576 reflections
171 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0366P)^2 + 1.434P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.31$ e Å^{-3}

Table 3
Selected geometric parameters (Å) for (II).

Mn1—O21	2.1100 (16)	Mn1—O2W	2.2381 (18)
Mn1—O1W	2.1639 (19)		

H atoms bonded to C atoms were refined with fixed individual displacement parameters [$U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$] using a riding model, with aromatic C—H distances of 0.95 Å. The H atoms bonded to O atoms in (II) were refined freely. The H atoms bonded to O atoms in (I) were refined using a riding model with fixed individual displace-

Table 4
Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1$\cdots$O21	0.96 (4)	1.59 (4)	2.478 (3)	153 (3)
O1W—H1$A\cdots$O22	0.85 (5)	1.97 (5)	2.760 (3)	154 (4)
O1W—H1$B\cdots$O2W^{i}	0.81 (4)	2.08 (4)	2.859 (3)	162 (4)
O2W—H2$A\cdots$O22$^{\text{ii}}$	0.74 (4)	1.97 (4)	2.691 (3)	165 (4)
O2W—H2$B\cdots$O1$^{\text{iii}}$	0.78 (3)	2.14 (4)	2.826 (3)	146 (3)

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

ment parameters [O—H = 0.84 Å and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(O)$]. The crystal of (I) is a non-merohedral twin. Two different domains could be identified when the crystal was on the diffractometer. The twin law (1 0 0.456/0 $\bar{1}$ 0/0 0 $\bar{1}$) was evaluated using the program *TWINLAW* (Bolte, 2004) and the reflection data file for refinement was prepared using the program *TWINLAW*. The highest peak in the final difference map of (I) is 1.46 Å from Mn1 and the deepest hole is 1.68 Å from O2W.

For both compounds, data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); publication software: *SHELXL97* and *PLATON* (Spek, 2003).

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