metal-organic compounds

Diaqua[N,N'-bis(5-methoxysalicyli-dene)ethylenediaminato-$\kappa^4 O$,N,N',O']-manganese(III) perchlorate, aqua-[N,N'-bis(3,5-dichlorosalicylidene)-ethylenediaminato-$\kappa^4 O$,N,N',O']-(methanol-κO)manganese(III) perchlorate and bis[μ-N,N'-bis-(3-methoxysalicylidene)ethylene-diaminato-$\kappa^5 O$,N,N',O':O]bis-[(methanol-κO)manganese(III)] diperchlorate

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The title compounds, a hydrogen-bonded linear chain, [Mn-($C_{18}H_{18}N_2O_4$)(H_2O)$_2$]ClO$_4$, (I), a hydrogen-bonded pseudo-dimer, [Mn($C_{16}H_{10}Cl_4N_2O_2$)(CH$_4$O)(H_2O)]ClO$_4$, (II), and a dimer, [Mn$_2$($C_{18}H_{18}N_2O_4$)$_2$(CH$_4$O)$_2$](ClO$_4$)$_2$, (III), respectively, have been structurally characterized. The three complexes are completely different in their structural features, despite identical counter-anions and only slight modification of the substituents in the ligands. Complex (I) affords an elongated octahedral coordination environment, with axial Mn—O(water) distances of 2.259 (3) and 2.313 (3) Å, which forms hydrogen-bonded linear chains along the crystallographic c axis. Hydrogen-bonded pseudo-dimeric compound (II) also affords an elongated octahedral coordination environment, with axial Mn—O(CH$_3$OH) = 2.222 (3) Å and Mn—O(water) = 2.266 (3) Å. Dimeric complex (III) is centrosymmetric and consists of distorted octahedral Mn atoms, with axial Mn—O(CH$_3$OH) = 2.242 (2) Å and Mn—O(phenolate) = 2.348 (1) Å, connected via bridging O atoms from one of the ligands. The magnetic properties of the three complexes are described.

Comment

Recently, photomagnetic functional complexes have been studied widely (Sato, 2003; Sato et $al.$, 2003). One of the hypotheses for the discovery of such materials is to examine complexes which exhibit ready structural changes and valence or spin transitions. For example, a certain Fe^{II} complex exhi-

bits spin-crossover due to Jahn–Teller distortion (Marchivie et $al.$, 2003; Kambara, 1979). Schiff base–Mn^{III} complexes have attracted considerable attention due to their catalysis and magnetism. Chiral catalysts are often employed for Kochi–Jacobsen–Katsuki enantioselective epoxidation (Korendovych & Rybak-Akimova, 2004; Martínez et $al.$, 2002; Reger & Janda, 2000; Khavrutskii et $al.$, 2003a,b). Various photo-catalytic reactions, including photocleavage of DNA (Saka-moto et $al.$, 1998), photophysical properties (Cozzi et $al.$, 2003) and photosystem II models (Ashmawy et $al.$, 1985; Aurangzeb et $al.$, 1994; Bermejo et $al.$, 1996), have been studied for many years. On the other hand, numerous dimeric high-spin Schiff base–Mn^{III} complexes exhibit ferromagnetism (Miyasaka et $al.$, 2002). These building blocks have potential in the design of new single-molecule magnets (Choi et $al.$, 2004), hydrogen-bonded assemblies (Wernsdorfer et $al.$, 2002) or multinuclear clusters (Mukhopadhyay et $al.$, 2004). However, axially compressed complexes undergoing the Jahn–Teller effect are rare for analogous Mn^{III} complexes (Shongwe et $al.$, 2001). The ^5D ground state may split into $^5T_{2g}$ and ^5E_g terms, and Jahn–Teller distortion removes the orbital degeneracy of the ^5E_g ground state to give the orbital singlet lowest in energy, either $^5A_{1g}$ or $^5B_{1g}$ (Kennedy & Murray, 1985). The spin degeneracy of the $^5A_{1g}$ or $^5B_{1g}$ states is further removed by spin-orbit coupling, which gives rise to zero-field splitting, D. Axial elongation results in the $^5B_{1g}$ level lying lowest with negative D, while axial compression leads to $^5A_{1g}$ with positive D. We present here three new Schiff base–Mn^{III} complexes, $viz.$ (I)–(III). Despite only slight modification of the substi-tuents and identical counter-anions, they are different in their dimeric features involving the axial coordination bonds. The three complexes are a hydrogen-bonded chain of pseudo-dimers, (I), a pseudo-dimer, (II), and a dimer, (III).
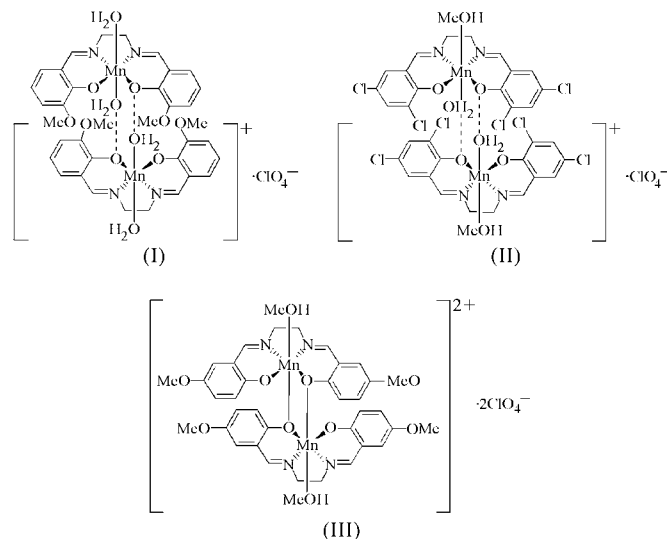

In complex (I) (Fig. 1), the central Mn^{III} ion adopts an elongated octahedral coordination geometry, with the displacement of the Mn1 ion from the O1/N1/N2/O2 least-squares plane being 0.012 (2) Å. Both axial sites are occupied by water ligands with a T value of 0.842, where $T = R_S/R_L$ denotes the ratio of equatorial and axial mean bond lengths undergoing

the Jahn–Teller effect (Hathaway & Billing, 1970). The disordered ethylenediamine moiety adopts a λ conformation, with an N1—C8A—C16A—N2 torsion angle of 48.3 (10)° [or N1—C8B—C16B—N2 = 46.0 (12)°]. The angle between the least-squares planes of the aromatic rings of the ligands is 4.43 (13)°.

In the crystal structure of (I), adjacent molecules are linked by hydrogen bonds [O5$\cdots$O3^i = 2.929 (3) Å, O5$\cdots$O1^i = 2.928 (3) Å, O5$\cdots$O4^i = 2.984 (3) Å, and O5$\cdots$O2^i = 2.949 (3) Å; symmetry code: (i) $1 - x$, $1 - y$, $1 - z$] to form hydrogen-bonded pseudo-dimers, with additional face-to-face π–π stacking interactions between the benzene groups (C5$\cdots$C9 = 3.54 Å and C4$\cdots$C10 = 3.56 Å). Furthermore, intermolecular hydrogen bonds [O6$\cdots$O8 = 3.029 (6) Å and O6$\cdots$O8^{ii} = 2.839 (6) Å; symmetry code: (ii) $1 - x$, $1 - y$, $2 - z$] between these pseudo-dimers and perchlorate counterions result in hydrogen-bonded linear chains along the crystallographic c axis. Finally, there is an additional edge-to-face interaction to the benzene group of a molecule adjacent to the linear chain (symmetry code: $1 - x$, $y - \frac{1}{2}$, $\frac{3}{2} - z$), with C4$\cdots$C10 = 3.30 Å.

In pseudo-dimeric complex (II) (Fig. 2), the central Mn^{III} ion also adopts an elongated octahedral coordination geometry, in which the displacement of the Mn1 ion from the O1/N1/N2/O2 least-squares plane is 0.029 (2) Å. The two axial ligands are water and methanol, and the mean T value is 0.866. The ethylenediamine moiety again adopts a λ conformation, with an N1—C8—C16—N2 torsion angle of 44.4 (4)°. Although the angle between the least-squares planes of the aromatic rings on both sides of the ligand is 3.00 (18)°, the overall molecular shape is a stepped conformation.
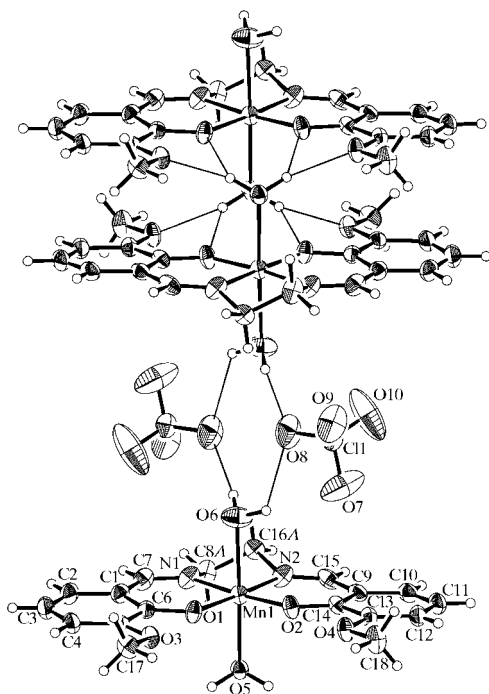
In the crystal structure of (II), adjacent molecules form centrosymmetric hydrogen-bonded pseudo-dimers [O4$\cdots$O1^{iii} = 2.845 (3) Å, O4$\cdots$O2^{iii} = 2.970 (4) Å, O4$\cdots$Cl2^{iii} = 3.270 (1) Å and O4$\cdots$Cl3^{iii} = 3.246 (3) Å; symmetry code: (iii) $1 - x$, $1 - y$, $-z$], with the shortest π–π stacking interaction between the benzene groups, viz. C4$\cdots$C13 = 3.42 Å. Moreover, hydrogen bonds [O3$\cdots$O7 = 2.834 (6) Å] are formed between the axial methanol ligand and the perchlorate ion.

As observed for (I) and (II), the Mn^{III} ion of dimeric complex (III) (Fig. 3) shows an elongated octahedral coordination geometry, which comprises the tetradentate Schiff base ligand. A methanol ligand occupies the outer axial site, while the phenolate O atom of the adjacent monomer occupies the inner axial site. The geometric parameters of the bridging moiety are O1—Mn1^{iv} = 2.348 (1) Å, O1—Mn1—O1^{iv} = 80.26 (5)°, Mn1—O1—Mn1^{iv} = 99.74 (5)° and Mn1$\cdots$Mn1^{iv} = 3.275 (1) Å [symmetry code: (iv) $1 - x$, $1 - y$, $1 - z$]. The displacement of the Mn1 ion from the O1/N1/N2/O2 least-squares plane is 0.055 (1) Å. The T values are 0.865 and 0.826 (average 0.846) for the methanol and phenolate O atoms, respectively. It should be noted that the in-plane coordination bond distance [Mn1—O1 = 1.921 (1) Å] is considerably longer than usual, because phenolate atom O1 also takes part in bridging, forming the dimers. The ethylenediamine moiety adopts a λ conformation, with an N1—C8—C16—N2 torsion angle of 44.9 (2)°. The angle between the least-squares planes of the aromatic rings of the ligands is 18.70 (7)°, which results from an overall stepped conformation.

In the crystal structure of (III), the perchlorate anions and dimers are packed alternately, with the shortest π–π stacking distance being between atom C1 and atom C14 in the adjacent benzene group (symmetry code: $1 - x$, $1 - y$, $1 - z$), of about 3.33 Å. An intramolecular hydrogen bond [O5$\cdots$O8 = 2.767 (3) Å] is formed between the axial methanol ligand and the perchlorate ion.
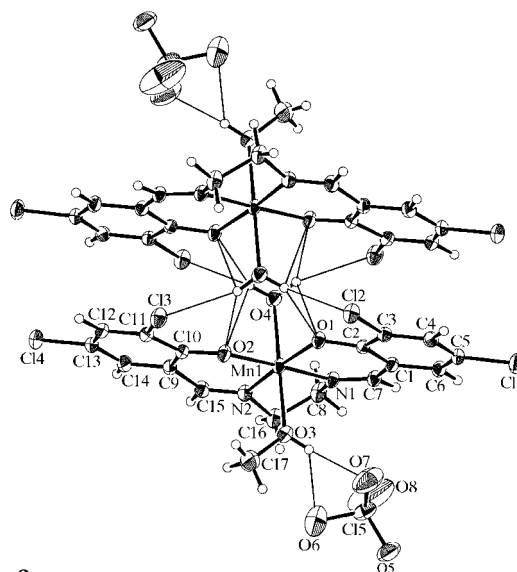

Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Thin lines indicate possible hydrogen bonds.

Figure 2
The molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Thin lines indicate possible hydrogen bonds.

The three complexes are quite different in their structural features. It is likely that substitution of the aromatic ring at the 5-position by methoxy in (I) and Cl in (II) prevents the formation of dimers, as seen for (III), and instead hydrogen-bonded pseudo-dimeric systems are formed. Indeed, both the steric and electronic features of Schiff base ligands, namely the electron-donating methoxy group and the electron-withdrawing Cl group, considerably influence the Jahn–Teller distortion of the axial Mn—O bonds. It is expected that electron-donating substituent groups result in a large Jahn–Teller elongation and ferromagnetism, due to the orthogonal e_g and $d\pi$ orbitals of the Mn^{III} ion.

The structural differences reflect the overall magnetic properties for compounds (I)–(III). The variable-temperature magnetic susceptibility was measured in the range 2–300 K, and the plot of effective magnetic moment *versus T* is given in Fig. 4. On lowering the temperature to about 50 K, the magnetic moment was kept almost constant for (I)–(III). It then gradually increased to more than 6 BM at 8 K and then decreased for (I), while (II) and (III) showed a decrease at about 20 K and reached less than 2 BM at 2 K. By analogy with related complexes (Saha *et al.*, 2004), the overall magnetic interaction of (I) is ferromagnetic, obeying $\chi = [Ng^2\beta^2/k(T-\alpha)][A/B]$, where $A = 30 + 14\exp(-8\,J/kT) +$

$5\exp(-14\,J/kT) + \exp(-18\,J/kT)$ and $B = 9 + 7\exp(-8\,J/kT) + 5\exp(-14\,J/kT) + 3\exp(-18\,K/kT) + \exp(-10\,J/kT)$, with the best-fit parameters of $J/K = 1.25$ K, $g = 1.99$, and $\alpha = -0.2$ K. The suitable geometry of the one-dimensional hydrogen-bonded chains of (I) results in a positive J value, which indicates ferromagnetic interaction. On the other hand, compounds (II) and (III) show antiferromagnetic interaction, indicating typical Curie–Weiss behaviour. The Weiss constants for (II) and (III) are -9.04 and -0.37 K, respectively. We attempted to analyse the data for (III) to obtain J. However, in contrast with many dimers, it is difficult to fit, because there is no inflection point in the plot of μ_{eff} versus T. Also, the treatment of the molecular field approximation is unclear. The diffuse reflectance spectra at 294 K support the $^5B_{1g}$ ground state of the Mn^{III} ion ($S = 2$) for (I)–(III).

In addition, we irradiated the crystals with UV and visible light at 8 K, which resulted in a reversible change of the IR band intensity around 3100 cm^{-1} (O—H band) for the axial ligands for (I)–(III). In contrast with the analogous Cu^{II} complex (Akitsu & Einaga, 2004), photo-irradiation did not affect the axial Jahn–Teller distortion for the three rigid Mn^{III} complexes (I)–(III).

Experimental

For (I), reaction of equimolar quantities of 5-methoxysalicylaldehyde (0.30 g, 2.00 mmol), ethylenediamine (0.30 g, 0.50 mmol) and manganese(III) acetate dihydrate (0.27 g, 1.00 mmol) in methanol (50 ml) at 323 K for 2 h gave a brown solution. After adding sodium perchlorate hydrate (0.70 g, 5.00 mmol) and stirring for 323 K for 1 h, the resulting solution was filtered and allowed to stand for two weeks at 298 K. Brown crystals of (I) suitable for X-ray crystallography were obtained from the filtrate. Analysis found: C 41.50, H 4.29, N 5.17%; calculated for $C_{18}H_{22}ClMnN_2O_{10}$: C 41.84, H 4.29, N 5.42%; IR (KBr): 1627 cm^{-1} (C=N band); m.p. 604 K (decomposition); UV–vis (diffuse reflectance): 13 300, 16 700 and 18 300 cm^{-1}; magnetic moment 4.77 BM at 294 K. For (II), the same preparation procedure was employed as given for (I), using 3,5-dichloro-salicylaldehyde (0.38 g, 2.00 mmol) instead of 5-methoxysalicylaldehyde. Analysis found: C 33.60, H 2.60, N 4.55%; calculated for $C_{34}H_{36}CuN_2O_4$: C 68.04, H 6.05, N 4.67%; IR (KBr): 1636 cm^{-1} (C=N); m.p. 542 K (decomposition); UV–vis (diffuse reflectance): 13 200 and 16 700 cm^{-1}; magnetic moment 4.54 BM at 294 K. For (III), the same preparation procedure was employed as given for (I), with 3-methoxysalicylaldehyde (0.30 g, 2.00 mmol) instead of 5-methoxysalicylaldehyde. Analysis found: C 44.50, H 4.29, N 5.17%; calculated for $C_{19}H_{22}ClMnN_2O_9$: C 44.50, H 4.32, N 5.46%; IR (KBr): 1621 cm^{-1} (C=N); m.p. 560 K (decomposition); UV–vis (diffuse reflectance): 18 300 cm^{-1}; magnetic moment 4.48 BM at 294 K.
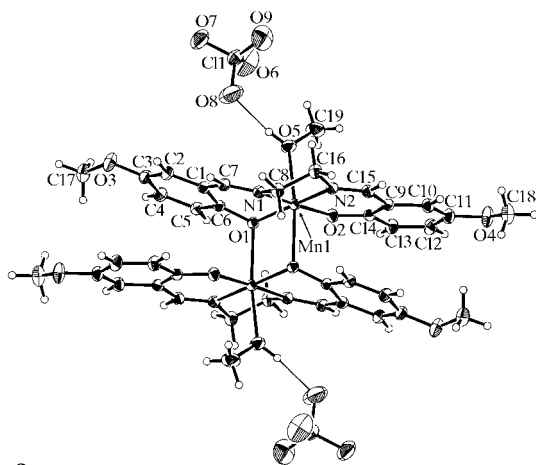

Figure 3
The molecular structure of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Thin lines indicate possible hydrogen bonds.
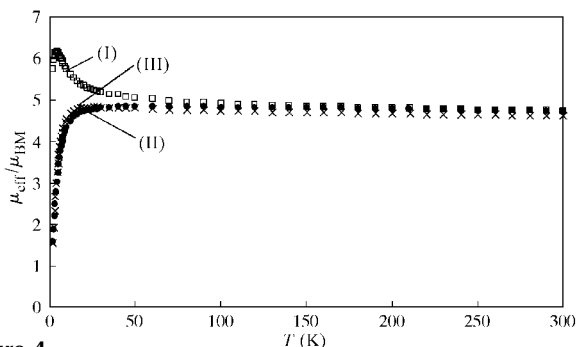

Figure 4
Plot of the effective magnetic moment *versus T* for (I)–(III), measured under 5000 G.

Compound (I)

Crystal data

$[Mn(C_{18}H_{18}N_2O_4)(H_2O)_2]ClO_4$	Mo $K\alpha$ radiation
$M_r = 516.77$	Cell parameters from 25
Orthorhombic, $Pbca$	reflections
$a = 22.751\,(9)$ Å	$\theta = 10.2–14.0°$
$b = 14.016\,(6)$ Å	$\mu = 0.80$ mm^{-1}
$c = 13.360\,(10)$ Å	$T = 297\,(2)$ K
$V = 4260\,(4)$ Å^3	Plate, brown
$Z = 8$	$0.46 \times 0.46 \times 0.10$ mm
$D_x = 1.611$ Mg m^{-3}	

Data collection

Rigaku AFC-7R diffractometer	$R_{int} = 0.000$
$\omega/2\theta$ scans	$\theta_{max} = 27.5°$
Absorption correction: ψ scan	$h = 0 \rightarrow 29$
(North *et al.*, 1968)	$k = -7 \rightarrow 18$
$T_{min} = 0.698$, $T_{max} = 0.923$	$l = -17 \rightarrow 7$
4892 measured reflections	3 standard reflections
4892 independent reflections	every 150 reflections
3324 reflections with $I > 2\sigma(I)$	intensity decay: 0.3%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1051P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.056$	$+ 1.1428P]$
$wR(F^2) = 0.174$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
3324 reflections	$\Delta\rho_{max} = 0.96$ e Å^{-3}
311 parameters	$\Delta\rho_{min} = -0.39$ e Å^{-3}
H-atom parameters constrained	

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

Mn1—O2	1.870 (2)	Mn1—N1	1.980 (3)
Mn1—O1	1.873 (2)	Mn1—O5	2.259 (3)
Mn1—N2	1.975 (3)	Mn1—O6	2.313 (3)
O2—Mn1—O1	92.88 (10)	N2—Mn1—O5	87.08 (12)
O2—Mn1—N2	92.73 (11)	N1—Mn1—O5	88.04 (11)
O1—Mn1—N2	174.36 (11)	O2—Mn1—O6	88.27 (13)
O2—Mn1—N1	174.58 (12)	O1—Mn1—O6	87.95 (13)
O1—Mn1—N1	92.10 (11)	N2—Mn1—O6	92.83 (14)
N2—Mn1—N1	82.32 (13)	N1—Mn1—O6	89.75 (14)
O2—Mn1—O5	93.95 (10)	O5—Mn1—O6	177.78 (11)
O1—Mn1—O5	91.92 (10)		

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O5—H5A⋯O3^i	0.96	2.09	2.929 (3)	145
O5—H5A⋯O1^i	0.96	2.12	2.928 (3)	140
O5—H5B⋯O4^i	0.96	2.12	2.984 (3)	150
O5—H5B⋯O2^i	0.96	2.18	2.949 (3)	136
O6—H6A⋯O8^{ii}	0.96	1.97	2.839 (6)	150
O6—H6B⋯O8	0.96	2.40	3.029 (6)	123

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

Compound (II)

Crystal data

[Mn(C$_{16}$H$_{10}$Cl$_4$N$_2$O$_2$)(CH$_4$O)-(H$_2$O)]ClO$_4$	$D_x = 1.786$ Mg m^{-3}
$M_r = 608.51$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 8.072$ (5) Å	$\theta = 10.0–14.4°$
$b = 21.270$ (10) Å	$\mu = 1.22$ mm^{-1}
$c = 13.712$ (7) Å	$T = 297$ (2) K
$\beta = 106.01$ (6)°	Prism, brown
$V = 2263$ (2) Å^3	0.60 × 0.30 × 0.30 mm
$Z = 4$	

Data collection

Rigaku AFC-7R diffractometer	$R_{int} = 0.072$
$\omega/2\theta$ scans	$\theta_{max} = 27.5°$
Absorption correction: ψ scan	$h = -10 \rightarrow 10$
(North *et al.*, 1968)	$k = 0 \rightarrow 27$
$T_{min} = 0.651$, $T_{max} = 0.693$	$l = 0 \rightarrow 17$
5879 measured reflections	3 standard reflections
5194 independent reflections	every 150 reflections
4367 reflections with $I > 2\sigma(I)$	intensity decay: 0.2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0722P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.046$	$+ 2.6279P]$
$wR(F^2) = 0.137$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
5194 reflections	$\Delta\rho_{max} = 1.24$ e Å^{-3}
298 parameters	$\Delta\rho_{min} = -0.99$ e Å^{-3}
H-atom parameters constrained	

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

Mn1—O1	1.897 (2)	Mn1—N1	1.990 (2)
Mn1—O2	1.902 (2)	Mn1—O3	2.222 (3)
Mn1—N2	1.985 (3)	Mn1—O4	2.266 (3)
O1—Mn1—O2	95.89 (10)	N2—Mn1—O3	89.81 (11)
O1—Mn1—N2	172.73 (10)	N1—Mn1—O3	90.35 (11)
O2—Mn1—N2	91.25 (11)	O1—Mn1—O4	91.41 (10)
O1—Mn1—N1	90.79 (10)	O2—Mn1—O4	90.62 (10)
O2—Mn1—N1	172.96 (9)	N2—Mn1—O4	87.14 (11)
N2—Mn1—N1	82.02 (11)	N1—Mn1—O4	86.98 (10)
O1—Mn1—O3	91.34 (10)	O3—Mn1—O4	176.20 (9)
O2—Mn1—O3	91.72 (10)		

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O3—H3⋯O7	0.84	2.00	2.834 (6)	174
O4—H4A⋯O1^i	0.84	2.08	2.845 (3)	151
O4—H4B⋯O2^i	0.84	2.30	2.970 (4)	137
O4—H4A⋯Cl2^i	0.84	2.71	3.270 (1)	126
O4—H4B⋯Cl3^i	0.84	2.51	3.246 (3)	147

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

Compound (III)

Crystal data

[Mn$_2$(C$_{18}$H$_{18}$N$_2$O$_4$)$_2$(CH$_4$O)$_2$]-(ClO$_4$)$_2$	$D_x = 1.603$ Mg m^{-3}
$M_r = 1025.55$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
$a = 15.226$ (6) Å	$\theta = 10.3–12.9°$
$b = 13.026$ (4) Å	$\mu = 0.80$ mm^{-1}
$c = 10.865$ (4) Å	$T = 297$ (2) K
$\beta = 99.58$ (3)°	Prism, brown
$V = 2124.9$ (13) Å^3	0.72 × 0.56 × 0.31 mm
$Z = 2$	

Data collection

Rigaku AFC-7R diffractometer	$R_{int} = 0.000$
$\omega/2\theta$ scans	$\theta_{max} = 27.5°$
Absorption correction: ψ scan	$h = -19 \rightarrow 19$
(North *et al.*, 1968)	$k = 0 \rightarrow 16$
$T_{min} = 0.589$, $T_{max} = 0.780$	$l = 0 \rightarrow 14$
4865 measured reflections	3 standard reflections
4865 independent reflections	every 150 reflections
4252 reflections with $I > 2\sigma(I)$	intensity decay: 0.2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0569P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$+ 0.9717P]$
$wR(F^2) = 0.101$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
4865 reflections	$\Delta\rho_{max} = 0.65$ e Å^{-3}
291 parameters	$\Delta\rho_{min} = -0.58$ e Å^{-3}
H-atom parameters constrained	

metal-organic compounds

Table 5
Selected geometric parameters (Å, °) for (III).

Mn1—O2	1.862 (1)	Mn1—O5	2.242 (2)
Mn1—O1	1.921 (1)	Mn1—O1^i	2.348 (1)
Mn1—N2	1.985 (2)	Mn1—Mn1^i	3.275 (1)
Mn1—N1	1.987 (2)		
O2—Mn1—O1	96.74 (6)	N1—Mn1—O5	90.55 (6)
O2—Mn1—N2	91.59 (6)	O2—Mn1—O1^i	91.38 (5)
O1—Mn1—N2	170.31 (6)	O1—Mn1—O1^i	80.26 (5)
O2—Mn1—N1	173.31 (6)	N2—Mn1—O1^i	94.65 (6)
O1—Mn1—N1	89.72 (6)	N1—Mn1—O1^i	87.96 (5)
N2—Mn1—N1	81.83 (7)	O5—Mn1—O1^i	172.17 (5)
O2—Mn1—O5	90.98 (6)	Mn1—O1—Mn1^i	99.74 (5)
O1—Mn1—O5	92.04 (6)	N1—C7—C1	124.42 (16)
N2—Mn1—O5	92.76 (7)	N2—C15—C9	125.25 (17)

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

Table 6
Hydrogen-bond geometry (Å, °) for (III).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H5$\cdots$O8	0.87	1.90	2.767 (3)	171

For (I), all H atoms were located in a difference Fourier map and allowed for using a riding model, with O—H = 0.96 Å and U_{iso}(H) = 1.2U_{eq}(O), and C—H = 0.93–0.97 Å and U_{iso}(H) = 1.2U_{eq}(C). There is positional disorder of atoms C8 and C16 over two equally occupied sites. It was assumed that the ethylenediamine moiety has two possible conformations, namely N1—C8A(H8$A$1/H8$A$2)—C16A-(H16A/H16B)—N2 and N1—C8B(H8$B$1/H8$B$2)—C16B(H16C/H16D)—N2. For (II), H atoms were placed in geometrically calculated positions and allowed for using a riding model, with O—H = 0.84 Å and U_{iso}(H) = 1.2U_{eq}(O), and C—H = 0.93–0.97 Å and U_{iso}(H) = 1.2U_{eq}(C). Atoms H17A–C and H17D–F, bound to methyl group C17, were modelled as idealized disordered groups with equal occupancy factors. For (III), H atoms were located in a difference Fourier map and allowed for using a riding model, with C—H = 0.93–0.97 Å and U_{iso}(H) = 1.2U_{eq}(C), except for atom H5, which was fixed in its difference map position. Atoms H19A–C and H19D–F, bound to methyl group C19, were modelled as idealized disordered groups with equal occupancy factors. Residual density greater than 1 e Å^{-3} is located 1.06, 1.35 and 1.13 Å from atoms O6, O7 and O8, respectively. The peaks indicate that there is slight disorder of these O atoms which has not been allowed for.

For all compounds, data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); structure solution: *SIR92* (Altomare *et al.*, 1994); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); publication software: *TEXSAN*.

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