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A novel one-dimensional complex: *catena*-poly[[manganese(III)-di-μ-2-[(2-hydroxyethyl)iminomethyl]phenolato-$\kappa^2O^1,N:\kappa O^2;\kappa O^2:\kappa^2O^1$] chloride]

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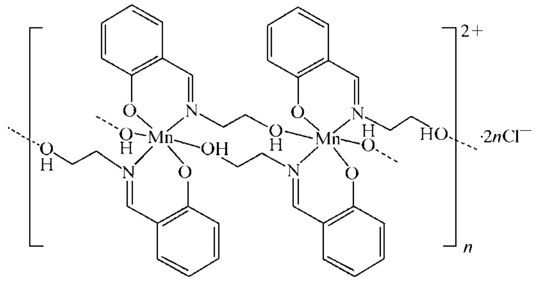
In the title one-dimensional complex, $\{[Mn^{III}(C_9H_{10}NO_2)_2]Cl\}_n$, the Schiff base ligand 2-[(2-hydroxyethyl)iminomethyl]phenolate ($Hsae^-$) functions as both a bridging and a chelating ligand. The Mn^{III} ion is six-coordinated by two N and four O atoms from four different $Hsae^-$ ligands, yielding a distorted MnO_4N_2 octahedral environment. Each $[Mn^{III}(Hsae)_2]^+$ cationic unit has the Mn atom on an inversion centre and each $[Mn^{III}(Hsae)_2]^+$ cation lies about another inversion centre. The chain-like complex is further extended into a three-dimensional network structure through Cl···H—O hydrogen bonds and C—H···π contacts involving the $Hsae^-$ rings.

Comment

Recently, the Schiff base proligand 2-[(2-hydroxyethyl)iminomethyl]phenol (H_2sae) and its derivatives have been employed to assemble discrete alkoxo- or phenoxo-bridged complexes with interesting magnetic properties in the field of coordination chemistry (Oshio *et al.*, 2000, 2003; Koizumi *et al.*, 2003). After deprotonation, H_2sae yields the potentially tridentate $Hsae^-$ or sae^{2-} ligands, which possess an ONO donor set and are able to bind in both bridging and chelating modes (Basler *et al.*, 2003). In addition, the favorable flexibility of the $–N{=}CH_2–CH_2–OH$ or $[–N{=}CH_2–CH_2–O]^-$ moiety and the rigidity of the benzene ring structure in $Hsae^-$ or sae^{2-} ligands can lead to unexpected complexes with beautiful molecular structures and interesting properties (Koizumi *et al.*, 2005). To date, more than 20 complexes involving Ni^{II}, Cu^{II}, Fe^{II}, Fe^{III}, Mn^{II} and Mn^{III} ions have been reported featuring $Hsae^-$ or sae^{2-} ligands and their derivatives (Dey *et al.*, 2002; Nihei *et al.*, 2003; Oshio, Nihei, Yoshida *et al.*, 2005; Boskovic *et al.*, 2003, 2005). It is noteworthy that several of these complexes exhibit the behavior of single-molecule magnets (SMMs) (Oshio *et al.*, 2004; Oshio, Nihei, Yoshida *et al.*, 2005; Oshio, Nihei, Koizumi *et al.*, 2005; Boskovic *et al.*, 2003). However, to the best of our knowledge, all such reported complexes are zero-dimensional, including mono- or binuclear complexes as well as polynuclear clusters. We report here the synthesis and crystal structure of a novel one-dimensional chain-like complex, $\{[Mn^{III}(Hsae)_2]Cl\}_n$, (I), which represents a new topology containing the $Hsae^-$ ligand.



(I)

The one-dimensional structure of (I) is depicted in Fig. 1, and selected bond lengths and angles are listed in Table 1. The crystal structure consists of a one-dimensional cationic polymer, $[Mn^{III}(Hsae)_2]_n^{n+}$, and free Cl^- anions. Each $[Mn^{III}(Hsae)_2]^+$ cationic unit is centrosymmetric. The Mn atom is six-coordinated symmetrically by two phenoxy O atoms and two N atoms from the two $Hsae^-$ ligands, and two alkoxy O atoms from the two adjacent $[Mn^{III}(Hsae)_2]^+$ units, yielding a distorted MnO_4N_2 octahedral surrounding. The Mn—O and Mn—N bond lengths are in accordance with the corresponding bonds in bi- or polynuclear complexes involving H_2sae or its derivatives (Table 2). In one $Hsae^-$ ligand, the phenoxo O atom and the N atom coordinate to the same Mn atom, whereas the alkoxo O atom coordinates to the next adjacent Mn atom. Alternatively, the complex can be simply considered as doubly linked by two O—C—C═N bridging groups (Fig. 1), which makes the one-dimensional structure look like an infinite '8'-shaped chain. The '8'-shaped chains are linked by Cl^- ions through O2—H10···Cl1 hydrogen bonds to form a two-dimensional network structure (Fig. 2). The networks are then further connected by C—H···π

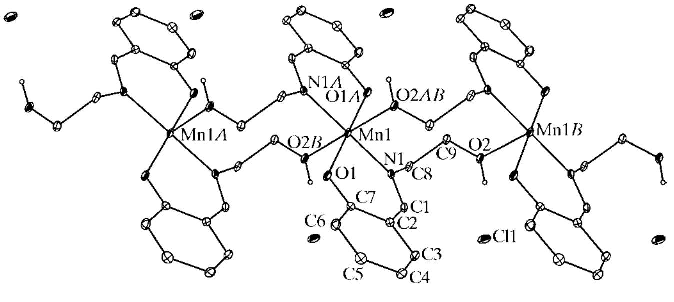


Figure 1
A fragment of the one-dimensional structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms bonded to C atoms have been omitted. [Symmetry codes on Mn: (*A*) *x*, *y* − 1, *z*; (*B*) *x*, *y* + 1, *z*; on N and O: (*A*) −*x*, −*y* + 1, −*z*; (*B*) *x*, *y* − 1, *z*; (*AB*) −*x*, −*y* + 2, −*z*.]

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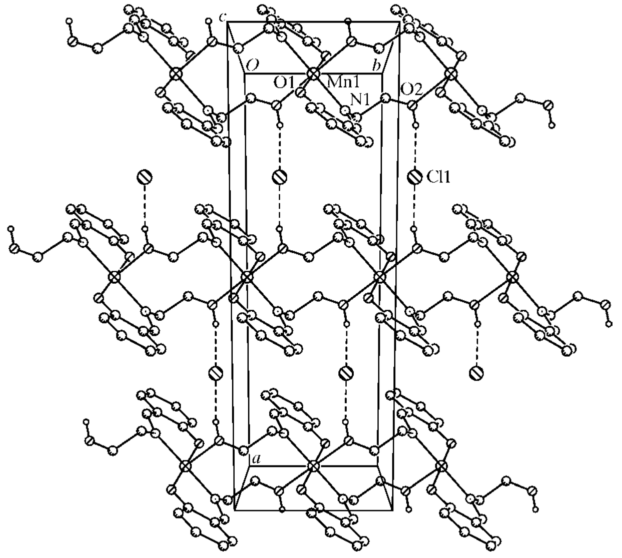

Figure 2
The two-dimensional network of (I), formed by hydrogen-bond interactions (along the c axis). Hydrogen bonds are shown as dashed lines and H atoms have been omitted for clarity.

contacts between the $Hsae^-$ rings, with a shortest CH$\cdots$C distance [C3—H3$\cdots$C4($-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$); Umezawa *et al.*, 1998] of 2.726 Å, to yield a three-dimensional non-covalent network structure.

Comparing with the reported alkoxo- or phenoxo-bridged polynuclear complexes containing the $Hsae^-$ or sae^{2-} ligand, we found that the key factor favoring the formation of a one-dimensional structure in the title complex, instead of a polynuclear structure, is that the phenoxo or alkoxo O atom does not act as a bridging atom, while the whole $Hsae^-$ ligand functions as a bridging group. The synthesis of the title complex is similar to that of the tetranuclear $[Mn_4(Hsae)_4Cl_4]$ complex (Boskovic *et al.*, 2003), except that a different solvent is used; this fact demonstrates that the molecular structures of complexes are strongly dependent on the solvent employed for the system.

Experimental

$MnCl_2·4H_2O$ (0.61 g, 3.09 mmol) was added to a solution of H_2sae (0.51 g, 3.09 mmol) in EtOH (40 ml), and the resulting mixture was stirred overnight and filtered. The filtrate was evaporated to dryness and then dissolved in a mixture of MeOH and MeCN (volume ratio about 1:4). The resulting solution was evaporated at room temperature until dark-brown needles formed.

Crystal data

$[Mn(C_9H_{10}NO_2)_2]Cl$
$M_r = 418.76$
Monoclinic, $C2/c$
$a = 18.202$ (8) Å
$b = 5.700$ (2) Å
$c = 18.703$ (9) Å
$\beta = 112.091$ (3)°
$V = 1797.9$ (13) Å^3
$Z = 4$
$D_x = 1.547$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2054 reflections
$\theta = 3.8$–27.5°
$\mu = 0.91$ mm^{-1}
$T = 123$ (2) K
Needle, brown
0.30 × 0.10 × 0.03 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
Oscillation scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.802$, $T_{max} = 0.928$
6807 measured reflections
2054 independent reflections
1571 reflections with $I > 2\sigma(I)$
$R_{int} = 0.092$
$\theta_{max} = 27.5°$
$h = -23 \rightarrow 23$
$k = -7 \rightarrow 6$
$l = -19 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.103$
$S = 0.96$
2054 reflections
122 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0254P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—O1	1.8659 (17)	Mn1—O2^i	2.2874 (15)
Mn1—N1	2.0232 (18)		
O1—Mn1—N1	89.32 (7)	N1—Mn1—O2^i	87.29 (7)
O1—Mn1—O2^i	88.56 (7)		

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

Table 2
Comparative geometric parameters (Å) for complexes involving similar ligands.

Complex	Mn—O$_{phenoxy}$	Mn—O$_{alkoxy}$	Mn—N
(I)^a	1.8659 (17)	2.2874 (15)	2.0232 (18)
(II)^b	1.856 (2)–1.866 (2)	–	1.972(3)–1.994 (3)
(III)^c	–	2.214 (2)–2.223 (3)	–
(IV)^d	1.882 (4)–2.100 (4)	–	1.968 (2)–2.228 (4)
(V)^e	1.860 (5)	–	2.021 (7)

† Notes: (*a*) this work; (*b*) $Mn_4Cl_4L_4$ (H_2L is salicylidene-2-ethanolamine; Boskovic *et al.*, 2003); (*c*) $Mn_2^{II}(H_2L)_2Cl_2$ [H_3L is *N*-(2-hydroxy-5-nitrobenzyl)iminodiethanol; Koizumi *et al.*, 2004]; (*d*) $[Mn_4^{II}Mn_2^{III}(sae)_6(CH_3OH)_2Cl_2]·2CH_3OH$ (H_2sae is 2-salicylideneaminoethanol; Hoshino *et al.*, 2003); (*e*) $Mn_2^{III}Ni_2^{II}Cl_2(salpa)_2$ [salpa is *N*-(2-hydroxybenzyl)-3-amino-1-propanol; Oshio, Nihei, Koizumi *et al.*, 2005].

The coordinates of the H atoms of the alkoxo group were found from difference Fourier maps and normalized to give an O—H distance of 0.85 Å. H atoms bound to C atoms were also visible in difference maps, and were positioned using the HFIX command in *SHELXL97* (Sheldrick, 1997) and refined as riding atoms (C—H = 0.97 or 0.93 Å).

Data collection: *CrystalStructure* (Rigaku/MSC, 2004); cell refinement: *CrystalStructure*; data reduction: *CrystalStructure*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Sheldrick, 1998); software used to prepare material for publication: *XP*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1257). Services for accessing these data are described at the back of the journal.

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