

cis-Dichloridobis(1,10-phenanthroline-5,6-diol- κ^2N,N')manganese(II): a supramolecular chain formed *via* O—H...Cl bonds and aromatic stacking

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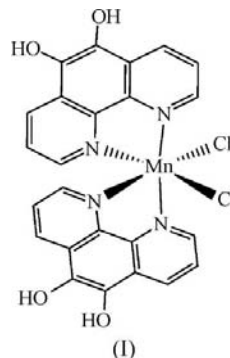
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The title compound, $[\text{MnCl}_2(\text{C}_{12}\text{H}_8\text{N}_2\text{O}_2)_2]$, displays a novel supramolecular chain formed by intermolecular O—H...Cl hydrogen bonds and aromatic stacking. The molecule has crystallographically imposed twofold symmetry with the Mn^{II} atom on the twofold axis. In the 1,10-phenanthroline-5,6-diol ligand, each H atom of the two hydroxy groups is oriented towards the other hydroxy O atom. Both hydroxy groups form intermolecular O—H...Cl hydrogen bonds with a single Cl atom of an adjacent molecule. These hydrogen bonds connect the molecules *via* operation of the molecular twofold axis and the centre of inversion of the crystal lattice, forming a doubly-bridged one-dimensional structure with Mn atoms as the nodes. Strong aromatic π -stacking between two antiparallel neighbouring 1,10-phenanthroline-5,6-diol ligands also helps to stabilize the chain.

Comment

In recent years there has been a rapidly increasing interest in the construction of various kinds of supramolecular systems for understanding molecular self-assembly principles and for designing molecular recognition devices. The term 'supramolecular system' generally refers to an assembly of molecules which are not covalently connected but assembled by other weak intermolecular interactions, such as hydrogen bonds and aromatic π - π stacking (Grabowski, 2005; Lehn, 1995; Pak *et al.*, 2005; Scheiner, 1997). Choosing appropriate ligands is essential in designing supramolecular systems. The rigid 1,10-phenanthroline-5,6-diol (phendiol) molecule is a versatile ligand from a structural point of view. The diimine group undoubtedly makes phendiol a strong chelating ligand. The diol groups can also easily function as another biting site upon deprotonation. Thus, phendiol can be either *N,N',O,O'*-tetradentate (Fox *et al.*, 1991; Ghosh *et al.*, 2005; Hill *et al.*, 1997;

Paw & Eisenberg, 1997; Paw *et al.*, 1998; Shavaleev *et al.*, 2003; Shukla & Das, 2000; Wu *et al.*, 2002), *N,N'*-bidentate (Ghosh *et al.*, 2005; Larsson & Ohrstrom, 2004; Murtaza *et al.*, 2002; Shukla & Das, 2000) or *O,O'*-bidentate (Ghosh *et al.*, 2005; Larsson & Ohrstrom, 2004; Murtaza *et al.*, 2002; Parsons *et al.*, 2006; Paw *et al.*, 1998; Shukla & Das, 2000). On the other hand, the planar fused-ring system makes it possible for phendiol to form π - π stacking interactions (Larsson & Ohrstrom, 2004). It is expected that the two hydroxy groups, if not deprotonated, may be able to act as intra/intermolecular hydrogen-bond donors or acceptors.



Although a number of phendiol-related complexes have been reported, until now the crystal structure of only one compound containing the neutral phendiol (not deprotonated) molecule has been determined. This compound is $[\text{Co}(\text{phendione})(\text{phendiol})_2]\text{Br}_3$ (phendione is 1,10-phenanthroline-5,6-dione), in which phendiol was created by slow hydration from phendione in $[\text{Co}(\text{phendione})_3]\text{Br}_3$ (Larsson & Ohrstrom, 2004). The bromide counter-anions bridge the phendiols *via* hydrogen bonds to form layers. The phendione fragment is not involved in hydrogen bonding, but is instead inserted in the cavity between two phendiol ligands. We report here the synthesis and characterization of *cis*- $[\text{MnCl}_2(\text{phendiol})_2]$, (I), in which an interesting one-dimensional bridged structure is present through an intermolecular hydrogen-bond network between the phendiol hydroxy groups and chloride ligands; there is also stacking of the phendiol groups.

The crystal structure indicates that the phendiol ligand was not deprotonated, despite the fact that the amount of MnCl_2 used was more than twice that of phendiol, which might favour phendiol acting as a bridging ligand; the hydrothermal method also usually favours the formation of water-insoluble metal-organic frameworks. We speculate that the acidity of MnCl_2 and the O—H...Cl hydrogen bonds helped to prevent the hydroxy groups from being deprotonated. The reaction of MnCl_2 and phendiol under ambient conditions also produced the title complex, as confirmed by IR. The IR spectrum of the free phendiol shows a broad and strong O—H band at 2972 cm^{-1} , indicative of intermolecular hydrogen bonding between the hydroxy groups. For (I), the O—H band moves upwards to 3301 cm^{-1} and is weaker, implying that the hydroxy groups of the phendiol ligand remain uncoordinated and the hydrogen bonding is weakened. This is consistent with the crystal structure analysis (see below), as the intermolecular O—H...Cl bonds replace the relatively stronger O—H...O

interaction in the free ligand. The IR band at 411 cm^{-1} for the complex but not the ligand is ascribed to the Mn–N coordination bond.

The neutral compound (I) crystallizes without disorder or solvent. The molecule exhibits C_2 symmetry with the Mn^{II} atom located on the twofold axis. As shown in Fig. 1 and Table 1, the Mn^{II} atom is hexacoordinated in a distorted octahedral geometry surrounded by four N atoms from two phendiol molecules and two Cl^- anions. The four ligands surround the central atom in a *cis* configuration. The geometric parameters of the coordinated phendiol are close to those in the only structurally characterized phendiol complex, *viz.* $[\text{Co}(\text{phendione})(\text{phendiol})_2]\text{Br}_3$ (Larsson & Ohrstrom, 2004). It is also worth comparing the structural features of the title compound with those of *cis*- $[\text{MnCl}_2(\text{phen})_2]$ (phen is 1,10-phenanthroline), which has been studied several times by X-ray diffraction (Malinowski *et al.*, 1996; McCann *et al.*, 1998; Zhou *et al.*, 1997). The Mn–N bond lengths in (I) exhibit two different values, reflecting the *trans* influence. Cl^- is a π -donor and 1,10-phenanthroline-like polypyridines are π -acceptors. Thus, the N atom *trans* to the phendiol N atom is a little closer

to the Mn^{II} atom than that *trans* to Cl^- . These two Mn–N bonds are both shorter than the corresponding bonds in *cis*- $[\text{MnCl}_2(\text{phen})_2]$, which are in the ranges 2.281–2.295 and 2.368–2.371 Å *trans* to the imine N atom and the Cl atom, respectively. The reasons for this might be that the donating hydroxy groups on the phendiol ligand strengthen the Mn–N bond through the fused ring system. Accordingly, the Mn–Cl bond length in (I) is greater than that in *cis*- $[\text{MnCl}_2(\text{phen})_2]$ (2.436–2.454 Å).

Both H atoms of the hydroxy groups in the phendiol ligand were located in a Fourier difference map. It is interesting that each of the two H atoms orients towards the adjacent hydroxy O atom, although their separation is quite short (1.95 Å). The two hydroxy groups in each phendiol ligand form intermolecular O–H...Cl hydrogen bonds with a single Cl atom of an adjacent molecule that is related by a centre of inversion (Table 2). The O–H...Cl hydrogen-bond data found here are comparable with those found in the literature (Fielden *et al.*, 2006; George *et al.*, 2006; Venegas-Yazigi *et al.*, 2006; Wong *et al.*, 2006). The four O–H...Cl hydrogen bonds about each inversion centre form a ring containing two Mn^{II} atoms, two Cl atoms and two phendiol ligands (Fig. 2). Through operation of the twofold axes through the Mn^{II} atoms, these rings are linked and expanded to a doubly-bridged chain structure in the [001] direction, with the Mn atoms as the nodes (Fig. 2). In pairs of inversion-related molecules, the two antiparallel phendiol ligands overlap in an offset face-to-face geometry. There is strong aromatic π -stacking between the two phendiol ligands. The ring planes are separated by 3.3456 (7) Å. The distance between the centroids of the central benzene rings of the two phendiol ligands is 3.4135 (10) Å. These parameters are typical of π - π interactions and are among the strongest of such interactions (Janiak, 2000; Russell *et al.*, 2001). This aromatic π -stacking force is undoubtedly another important factor in the stabilization of the chain structure. There is no remarkable interaction between the chains.

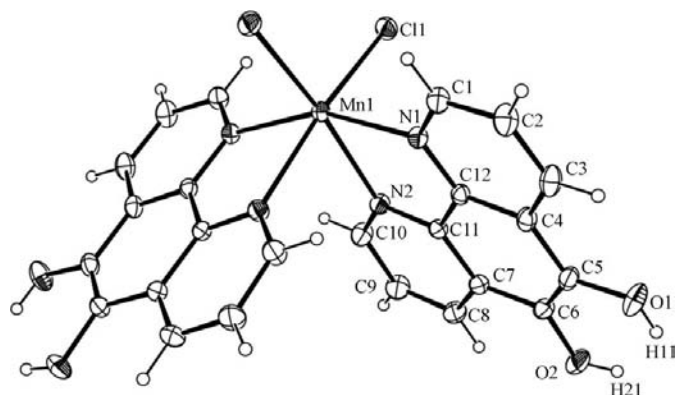


Figure 1
A view of the molecule of (I), showing the atom numbering of the structurally unique non-H atoms and the hydroxy H atoms. Displacement ellipsoids are shown at the 25% probability level.

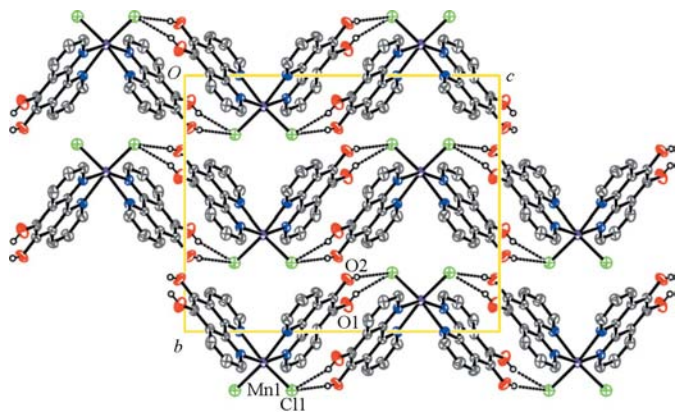


Figure 2
The packing of (I), viewed down the *a* axis. H atoms have been omitted for clarity, except for those attached to O atoms. Dashed lines indicate intermolecular O–H...Cl hydrogen bonds.

Experimental

1,10-Phenanthroline-5,6-diol (phendiol) was prepared from 1,10-phenanthroline-5,6-dione according to our previously reported method (Wu *et al.*, 2002). Phendiol (0.0646 g, 0.3 mmol) and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.1686 g, 0.85 mmol) were mixed with water (10 ml) and sealed in a 15 ml stainless steel bomb with a Teflon liner and heated at 433 K for 50 h. After cooling to room temperature, brown block-shaped crystals were obtained (yield 0.0725 g, 88%, based on the ligand). Analysis found: C 52.54, H 2.82, N 10.36%; $\text{C}_{24}\text{H}_{16}\text{Cl}_2\text{MnN}_4\text{O}_4$ requires: C 52.39, H 2.93, N 10.18%. IR (ν_{max} , cm^{-1}): 3301 (*br/m*), 1625 (*s*), 1591 (*m*), 1429 (*m*), 1315 (*m*), 1123 (*m*), 1064 (*s*), 1025 (*s*), 818 (*s*), 734 (*s*), 411 (*m*).

Crystal data

$[\text{MnCl}_2(\text{C}_{12}\text{H}_8\text{N}_2\text{O}_2)_2]$
 $M_r = 550.25$
Monoclinic, $C2/c$
 $a = 8.5272$ (2) Å
 $b = 14.4503$ (4) Å
 $c = 18.1776$ (5) Å
 $\beta = 101.777$ (2)°

$V = 2192.70$ (10) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.89\text{ mm}^{-1}$
 $T = 293$ (2) K
 $0.23 \times 0.21 \times 0.20\text{ mm}$

Data collection

Bruker APEXII area-detector diffractometer
9077 measured reflections
2600 independent reflections
2350 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.082$
 $S = 1.03$
2600 reflections
161 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.59 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.27 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Mn1—N1	2.2359 (14)	Mn1—Cl1	2.4938 (5)
Mn1—N2	2.3039 (14)		
N1 ⁱ —Mn1—N1	157.37 (8)	N2 ⁱ —Mn1—Cl1	167.04 (4)
N1—Mn1—N2 ⁱ	88.85 (5)	N2—Mn1—Cl1	90.04 (4)
N1—Mn1—N2	73.61 (5)	N1—Mn1—Cl1 ⁱ	99.22 (4)
N2 ⁱ —Mn1—N2	79.19 (7)	N2—Mn1—Cl1 ⁱ	167.04 (4)
N1—Mn1—Cl1	95.05 (4)	Cl1—Mn1—Cl1 ⁱ	101.49 (3)

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

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H11 ⁱⁱ ···Cl1 ⁱⁱ	0.82	2.42	3.2020 (16)	161
O2—H21 ⁱⁱ ···Cl1 ⁱⁱ	0.82	2.41	3.2042 (16)	163

Symmetry code: (ii) $-x + 2, -y + 2, -z + 1$.

All H atoms were located in difference maps and then treated as riding atoms in geometrically idealized positions, with C—H distances of 0.93 \AA and O—H distances of 0.82 \AA , and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{O})$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3111). Services for accessing these data are described at the back of the journal.

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