Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

catena-Poly[4,4′-bipyridinium [[*cis*-dichloromanganese(II)]-di-μ-chloro]], a novel manganese(II) coordination polymer with 4,4′-bipyridinium

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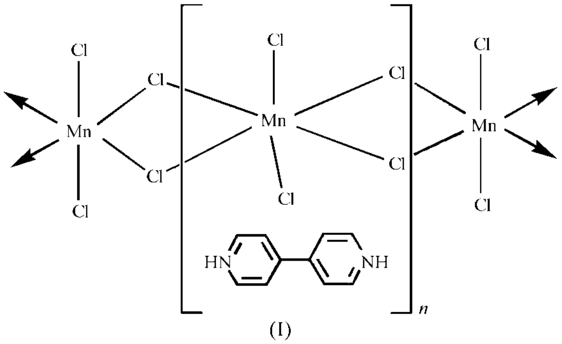
Received 31 August 2006
Accepted 18 September 2006
Online 19 October 2006

The title novel manganese(II) coordination polymer, $\{(C_{10}H_{10}N_2)[MnCl_4]\}_n$, consists of a one-dimensional infinite zigzag chain composed of polymeric $[MnCl_4]^{2-}$ units in which each Mn^{2+} ion is located on a twofold rotation axis and is coordinated to two terminal Cl atoms and four bridging chloro ligands. Adjacent Mn^{2+} ions are linked by double Cl bridges arranged about a centre of inversion, thus forming anionic chains of distorted edge-sharing octahedra. Rows of approximately parallel 4,4′-bipyridinium cations run side-by-side with the $MnCl_4$ chains. A two-dimensional layer structure is constructed *via* hydrogen bonds and by additional π–π stacking interactions.

Comment

Polymeric manganese chloride compounds with fascinating topological chemistry have aroused considerable interest (Law *et al.*, 1998; Yachandra *et al.*, 1996). In these studies, bipyridine (bipy) and bipyridine-related ligands play a key role in constructing the structures. Since $MnCl_3L$ compounds (L is bipy and phenanthroline) were isolated from the reaction of L with the purple ether extract of the black solid obtained from the reduction of MnO_2 with dry HCl in CCl_4 by Goodwin & Sylva (1965), similar compounds have been reported (Lubben *et al.*, 1995; Perlepes *et al.*, 1991; Lumme & Lindell, 1988; Wang *et al.*, 2005). To date, however, manganese chloride polymers with 4,4′-bipyridine molecules have not been reported. We present here for the first time the structure of a novel manganese chloride polymer containing diprotonated 4,4′-bipyridine, *viz.* $\{(H_2bipy)[MnCl_4]\}_n$, (I).



(I)

The molecular structure of (I) is shown in Fig. 1. The crystal structure contains polymeric $[MnCl_4]^{2-}$ units, which are linked to each other through two bridging chloro ligands between adjacent centrosymmetrically-related Mn sites to construct one-dimensional infinite zigzag chains, and groups of isolated C_2-symmetric 4,4′-bipyridinium cations with an approximately parallel arrangement (Fig. 2). The Mn^{2+} ion is coordinated by six Cl atoms, with Mn—Cl distances ranging from 2.4935 (4) to 2.6579 (3) Å and Cl—Mn—Cl angles deviating from 90 or 180° by 4–11° (Table 1), indicating a moderately distorted octahedral geometry. The $MnCl_6$ octahedra have C_2 symmetry and are edge-shared to form a one-dimensional infinite chain extending along the *a* axis. Columns of diprotonated 4,4′-bipyridine molecules pack in alternating rows side-by-side with the one-dimensional chains. In the diprotonated 4,4′-bipyridine unit, the dihedral angle between the bipy rings is 21.18 (6)°, which is comparable to the dihedral angle of 23.4° in $[(H_2NCH_2CONHCH_2COO)Cu(OH)(C_{10}H_8N_2)Cu(OH)_2(H_2NCH_2CONHCH_2COO)]\cdot 9H_2O$ (Wang *et al.*, 1994). There

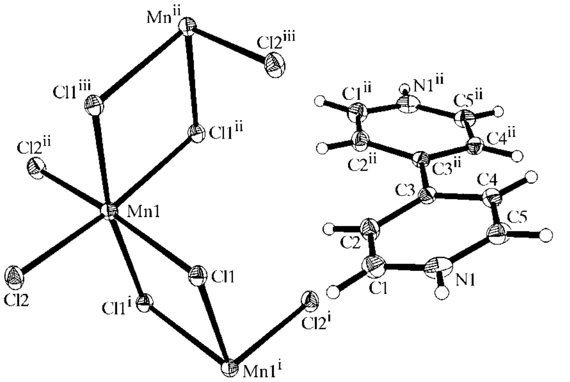


Figure 1
A view of the molecular structure of (I), showing the atom-numbering scheme. Symmetry-equivalent Cl atoms have been included to show the complete coordination sphere of the Mn cation. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $-x-1, -y, -z+1$; (ii) $-x-\frac{3}{2}, y, -z+1$; (iii) $x-\frac{1}{2}, -y, z$.]

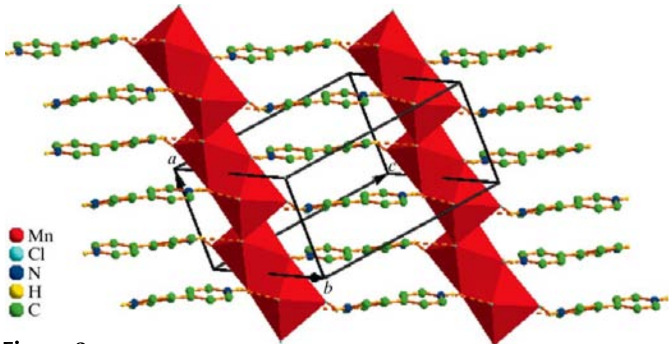


Figure 2
The two-dimensional layer structure of (I). Hydrogen bonds are indicated by dashed lines.

DOI: 10.1107/S0108270106038108

are N—H···Cl hydrogen-bond interactions between the isolated 4,4′-bipyridinium cations and the manganese chloride chains (Table 2). In addition, the alternate stacking of the rings of the bipy molecules results in ring separations ranging from 3.5 to 4.4 Å, indicating weak π–π stacking interactions. As shown in Fig. 2, it is believed that these hydrogen-bonding and π–π interactions may play an important role in stabilizing the two-dimensional layer structure of (I).

Experimental

All reagents and solvents were used as obtained without further purification. An aqueous solution (50 ml) containing $Na_2MoO_4{\cdot}2H_2O$ (14.5 g), whose pH was adjusted to 4.5 with concentrated HNO_3 solution, was added to an aqueous solution (4 ml) containing $MnCl_2{\cdot}4H_2O$ (1.98 g). The resulting mixture was stirred for 12 h and then filtered. Yellow crystals (0.2 g) were collected, redissolved in water (20 ml), and then added to an aqueous solution (20 ml) containing $CrCl_3{\cdot}6H_2O$ (0.3 g), CH_3CH_2OH (10 ml) and 4,4′-bipyridine (0.7 g). The resulting mixture was stirred for 2 h and filtered. Yellow crystals of (I) were collected after a few days. The formation of this compound appears to be a chance event and attempts to synthesize it in the absence of $Na_2MoO_4{\cdot}2H_2O$ and $CrCl_3{\cdot}6H_2O$ have so far been unsuccessful.

Crystal data

$(C_{10}H_{10}N_2)[MnCl_4]$
M_r = 354.95
Monoclinic, $I2/a$
a = 6.9781 (6) Å
b = 12.7118 (13) Å
c = 14.1568 (14) Å
β = 91.206 (2)°
V = 1255.5 (2) Å^3

Z = 4
D_x = 1.878 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 1.88 mm^{-1}
T = 293 (2) K
Block, yellow
0.26 × 0.19 × 0.17 mm

Data collection

Rigaku R-AXIS-IV diffractometer
ω scans
Absorption correction: empirical (using intensity measurements) (*ABSCOR*; Higashi, 1995)
$T_{\min}$ = 0.643, $T_{\max}$ = 0.745

4519 measured reflections
1105 independent reflections
1085 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.018
$\theta_{\max}$ = 25.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.015
$wR(F^2)$ = 0.044
S = 1.04
1105 reflections
79 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.027P)^2 + 0.6644P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.25 e Å^{-3}
$\Delta\rho_{\min}$ = −0.18 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0071 (5)

H atoms were placed in idealized positions and allowed to ride on their parent atoms, with $U_{\rm iso}$(H) values fixed at $1.2U_{\rm eq}$ of the parent C and N atoms, and with C—H distances of 0.93 Å and an N—H distance of 0.86 Å.

Data collection: *PROCESS-AUTO* (Rigaku, 2002); cell refinement: *PROCESS-AUTO* (Rigaku, 2002); data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *WinGX* (Farrugia, 1999); software used to prepare material for publication: *SHELXL97*.

Table 1
Selected geometric parameters (Å, °).

Mn1—Cl2	2.4935 (4)	Mn1—Cl1$^{\rm i}$	2.6579 (3)
Mn1—Cl1	2.6018 (4)		
Cl2—Mn1—Cl2$^{\rm ii}$	93.119 (18)	Cl1—Mn1—Cl1$^{\rm i}$	79.581 (12)
Cl2—Mn1—Cl1$^{\rm ii}$	170.603 (10)	Cl2—Mn1—Cl1$^{\rm iii}$	91.023 (12)
Cl2—Mn1—Cl1	87.992 (12)	Cl1—Mn1—Cl1$^{\rm iii}$	93.213 (11)
Cl1$^{\rm ii}$—Mn1—Cl1	92.435 (16)	Cl1$^{\rm i}$—Mn1—Cl1$^{\rm iii}$	169.651 (17)
Cl2—Mn1—Cl1$^{\rm i}$	96.095 (12)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···Cl2$^{\rm iv}$	0.86	2.54	3.2042 (12)	135
N1—H1A···Cl1$^{\rm iv}$	0.86	2.60	3.2468 (12)	132

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

Financial support from the Program for New Century Excellent Talents at the University of Henan Province, the Institute of Education of Henan Province and the Natural Science Foundation of Henan Province is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3038). Services for accessing these data are described at the back of the journal.

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