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Bis(piperazinium) di-μ-chloro-bis[diaqua-dichloromanganate(II)] dichloride

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The title compound, $(C_4H_{12}N_2)_2[Mn_2Cl_6(H_2O)_4]Cl_2$, consists of two piperazinium cations, two chloride anions and a dimanganese complex anion, which lies on a center of symmetry. Each Mn^{II} atom is located in a distorted octahedral environment. The cations and the anions are held together by O—H···Cl and N—H···Cl hydrogen bonds. The structure features the formation of inorganic and organic ionic layers, which interpenetrate each other and which are linked by hydrogen bonds.

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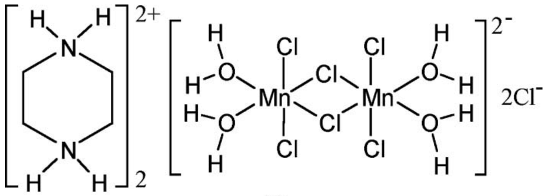
Key indicators

Single-crystal X-ray study
T = 299 K
Mean σ(C–C) = 0.003 Å
R factor = 0.023
wR factor = 0.057
Data-to-parameter ratio = 14.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The chloride anion, as a bridging ligand, exhibits a good binding ability in the formation of coordination complexes (Caneschi *et al.*, 1990; Fryzuk *et al.*, 1994; Rancurel *et al.*, 2000; Wang *et al.*, 2003). Piperazine is a strong basic amine which readily forms dications, where all four N—H bonds are generally active in hydrogen-bond formation (Coupar *et al.*, 1996; Ferguson *et al.*, 1998). Moreover, dinuclear manganese complexes are active in biological redox reactions involving water, peroxide and dioxygen (Barynin *et al.*, 1997; Zhang *et al.*, 2001). Recently, we have synthesized the title compound, (I), a dinuclear manganese(II) complex.



(I)

The title compound consists of two diprotonated piperazinium ions, two chloride anions and a dimanganese(II) anion (Fig. 1). The Mn^{II} complex is built up from two inver-

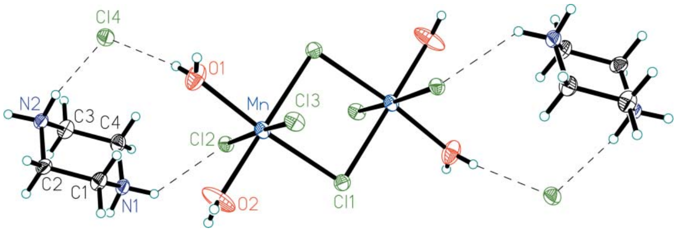


Figure 1
The formula unit with atom labels, showing 40% probability displacement ellipsoids. Unlabeled atoms are related by the symmetry code ($-x$, $-y$, $1 - z$). Hydrogen bonds are illustrated as dashed lines.

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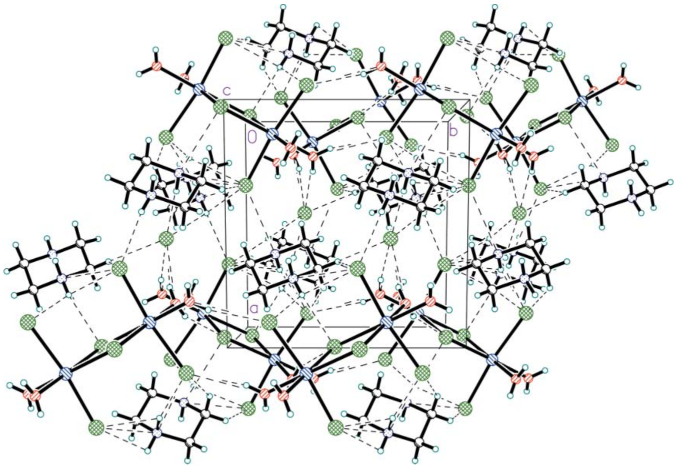

Figure 2
The packing, viewed down along the *c* axis. Hydrogen bonds are shown as dashed lines.

sion-related Mn^{II} atoms bridged by two Cl^- anions, where the Mn—Cl—Mn bond angle is 94.41 (2)°, smaller than the value of 96.82 (4)° in the pentacoordinated dimanganese compound $[MnCl_2(HDPhF)_2]_2$ (HDPhF is diphenylformamidine) (Arnold *et al.*, 1997). The Mn^{II} atoms in (I) are separated by a distance of 3.843 (7) Å, which is quite large and seems to rule out any strong direct metal–metal interaction. Each Mn^{II} atom is located in a distorted octahedral environment; the equatorial plane is formed by coordinated atoms O1, O2, Cl1 and Cl1($-x$, $-y$, $1 - z$). The O2 water molecule is firmly bonded to the Mn^{II} atom, with a bond length of 2.1776 (18) Å, which is one of the shortest such lengths observed (Orpen *et al.*, 1989; Garoufis *et al.*, 1999). The bridging Mn—Cl bonds, *viz*. Mn—Cl1 and Mn—Cl1($-x$, $-y$, $1 - z$), are obviously elongated, while the terminal Mn—Cl2 and Mn—Cl3 bonds are normal for hexacoordinated Mn^{II} complexes (Orpen *et al.*, 1989).

In the structure of (I), a piperazinium cation is linked to an uncoordinated chloride ion by an N2—H2N*B*···Cl4 hydrogen bond, and the chloride ion is, in turn, linked to a coordinated water molecule by an O1—H1O*A*···Cl4 hydrogen bond (Fig. 1 and Table 2). In addition, the cation is linked to a coordinated Cl atom by an N1—H1N*A*···Cl2 hydrogen bond. The hydrogen bonds mentioned above result in a supramolecular ring, which may be described by the graph set $R_2^3(11)$ (Etter, 1990; Grell *et al.*, 2000). As shown in Fig. 2, the structure features inorganic and organic ionic layers parallel to the (100) plane, which interpenetrate and are linked by hydrogen bonds (Table 2).

Experimental

Piperazine, $MnCl_2$ and HCl in a molar ratio of 1:2:4 were mixed, dissolved in water and heated to a temperature where a clear solution resulted. Single crystals of (I) formed when the solution was left standing overnight at 293 K. IR (KBr, cm^{-1}): 3441 (*b*), 3008 (*w*), 2995 (*w*), 2748 (*m*), 2459 (*w*), 1629 (*s*), 1464 (*m*), 1354 (*m*), 1234 (*m*), 1091 (*w*), 812 (*m*), 791 (*m*), 718 (*m*), 599 (*m*), 570 (*w*), 446 (*w*).

Crystal data

$(C_4H_{12}N_2)_2[Mn_2Cl_6(H_2O)_4]Cl_2$
$M_r = 641.86$
Monoclinic, $P2_1/c$
$a = 9.865$ (2) Å
$b = 9.429$ (1) Å
$c = 13.506$ (2) Å
$\beta = 101.74$ (1)°
$V = 1230.0$ (3) Å^3
$Z = 2$
$D_x = 1.733$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 36 reflections
$\theta = 5.2$–15.1°
$\mu = 1.92$ mm^{-1}
$T = 299$ (2) K
Block, pink
0.56 × 0.56 × 0.26 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\rm min} = 0.356$, $T_{\rm max} = 0.608$
2623 measured reflections
2235 independent reflections
1931 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.012$
$\theta_{\rm max} = 25.3°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 11$
$l = -16 \rightarrow 15$
3 standard reflections every 97 reflections intensity decay: 1.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.057$
$S = 1.09$
2235 reflections
151 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0296P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.26$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.23$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0331 (10)

Table 1
Selected geometric parameters (Å, °).

Mn—O2	2.1776 (18)	N1—C4	1.488 (3)
Mn—O1	2.2308 (18)	N1—C1	1.489 (3)
Mn—Cl2	2.4540 (7)	N2—C2	1.488 (3)
Mn—Cl3	2.5038 (7)	N2—C3	1.492 (3)
Mn—Cl1	2.5939 (7)	C1—C2	1.509 (3)
Mn—Cl1$^{\rm i}$	2.6429 (6)	C3—C4	1.507 (3)
O2—Mn—O1	91.14 (9)	O2—Mn—Cl1	93.56 (7)
O2—Mn—Cl2	86.86 (5)	Cl2—Mn—Cl1	90.36 (2)
O1—Mn—Cl2	91.21 (5)	Cl3—Mn—Cl1	92.32 (2)
O2—Mn—Cl3	86.35 (5)	Mn—Cl1—Mn$^{\rm i}$	94.41 (2)
O1—Mn—Cl3	86.66 (5)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O*A*···Cl4	0.81 (1)	2.40 (1)	3.197 (2)	167 (4)
O1—H1O*B*···Cl1$^{\rm ii}$	0.81 (1)	2.77 (2)	3.5411 (19)	160 (3)
O2—H2O*B*···Cl3$^{\rm iii}$	0.81 (1)	2.45 (1)	3.2433 (19)	167 (3)
O2—H2O*A*···Cl4$^{\rm iv}$	0.81 (1)	2.37 (1)	3.174 (2)	172 (3)
N1—H1N*A*···Cl2	0.89 (1)	2.50 (2)	3.168 (2)	132 (2)
N1—H1N*B*···Cl3$^{\rm v}$	0.89 (1)	2.39 (1)	3.223 (2)	156 (2)
N2—H2N*B*···Cl4	0.91 (1)	2.25 (1)	3.148 (2)	169 (2)
N2—H2N*A*···Cl1$^{\rm vi}$	0.90 (1)	2.49 (2)	3.247 (2)	141 (2)

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

H atoms attached to O and N atoms were located in a difference Fourier map and refined isotropically. Other H atoms were placed in calculated positions and allowed to ride on their parent atoms at a distance of 0.97 Å, with isotropic displacement parameters 1.2 times U_{eq} of the parent atoms.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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References

Arnold, D. I., Cotton, F. A., Maloney, D. J. & Matonic, J. H. (1997). *Polyhedron*, **16**, 133–141.

Barynin, V. V., Hempstead, P. D., Vagin, A. A., Antonyuk, S. V., Melik-Adamyan, W. R., Lamzin, V. S., Harrison, P. M. & Artymiuk, P. J. (1997). *J. Inorg. Biochem.* **67**, 196.

Caneschi, A., Ferraro, F., Gatteschi, D., Rey, P. & Sessoli, R. (1990). *Inorg. Chem.* **29**, 1756–1760.

Coupar, P. I., Ferguson, G. & Glidewell, C. (1996). *Acta Cryst.* C**52**, 3052–3055.

Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.

Ferguson, G., Glidewell, C., Gregson, R. M. & Meehan, P. R. (1998). *Acta Cryst.* B**54**, 129–138.

Fryzuk, M. D., Lezno., D. B., Rettig, S. J. & Thompson, R. C. (1994). *Inorg. Chem.* **33**, 5528–5534.

Garoufis, A., Kasselouri, S., Boyatzis, S. & Raptopoulou, C. P. (1999). *Polyhedron*, **18**, 1615–1620.

Grell, J., Bernstein, J. & Timhofer, G. (2000). *Acta Cryst.* B**56**, 166–179.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Orpen, A. G., Brammer, K., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1–S83.

Rancurel, C., Lezno., D. B., Sutter, J. P., Guionneau, P., Chasseau, D., Kliava, J. & Kahn, O. (2000). *Inorg. Chem.* **39**, 1602–1605.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. Version 97-1. University of Göttingen, Germany.

Siemens (1994). *XSCANS*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1998). *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Wang, L. Y., Zhang, C. X., Liu, Z. Q., Liao, D. Z., Jiang, Z. H. & Yan., S. P. (2003). *Inorg. Chem. Commun.* **6**, 1255–1258.

Zhang, J. J., Luo, Q. H., Duan, C. Y., Wang, Z. L. & Mei, Y. H. (2001). *J. Inorg. Biochem.* **86**, 573–579.