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cis-Dichlorobis(2,2′-diamino-4,4′-bi-1,3-thiazole)manganese(II) methanol solvate

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Key indicators

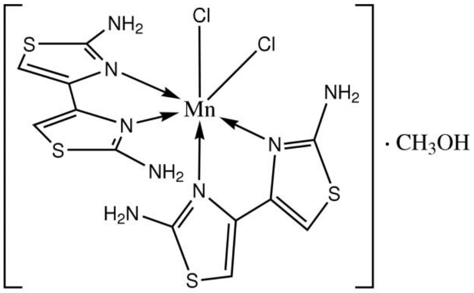
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.007 Å
R factor = 0.057
wR factor = 0.136
Data-to-parameter ratio = 15.2

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

In the title compound, $[MnCl_2(C_6H_6N_4S_2)_2]\cdot CH_3OH$, the Mn^{II} ion is coordinated by two 2,2′-diamino-4,4′-bithiazole ligands and two Cl$^-$ anions in *cis* positions to form a distorted octahedral coordination geometry. In the crystal structure, a three-dimensional supramolecular structure involving hydrogen bonding and aromatic packing is observed.

Comment

Some complexes of manganese have served as mimics for manganese catalases and extradiol-cleaving catechol dioxygenase (Triller *et al.* 2002, 2003). The five-membered heterocycles, thiazole and its derivatives, are common structural features of many biologically important natural products (Crosa & Walsh, 2002). Transition metal complexes with 2,2′-diamino-4,4′-bithiazole (DABT) or its derivatives have been found to be effective inhibitors of DNA synthesis in tumour cells (Fisher *et al.*, 1985; Waring, 1981). We describe here the crystal structure of the title complex, (I), an Mn^{II} complex with DABT.



(I)

The title compound comprises a neutral manganese complex and a methanol solvent molecule (Fig. 1). The complex molecule contains a six-coordinated Mn^{II} ion coordinated by two chelate DABT ligands and two Cl$^-$ anions at *cis* positions, and displays a distorted octahedral coordination geometry. Selected geometric parameters are listed in Table 1.

The DABT ligands are non-polar in the structure; the dihedral angle between the thiazole rings containing N1 and N2 is 10.8 (3)°, and that between the rings containing N5 and N6 is 7.6 (3)°. Both ligands coordinate to the Mn^{II} ion in the usual chelating bidentate mode, with bite angles of 74.07 (14) and 73.87 (13)°, respectively (Tian *et al.*, 1996; Luo *et al.*, 2004; Liu & Xu, 2005). Their mean planes are nearly perpendicular to one another [84.00 (8)°]. Such an arrangement facilitates intramolecular N—H···Cl and N—H···N hydrogen bonds (Table 2).

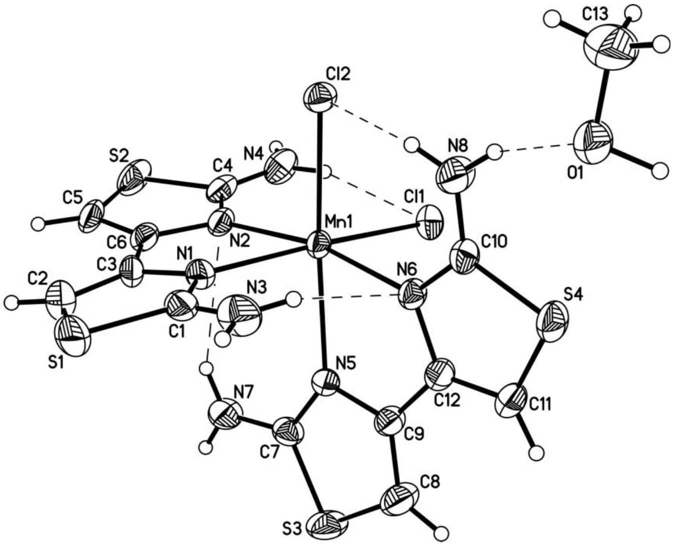


Figure 1
A view of the title compound. Displacement ellipsoids are drawn at the 30% probability level. Dashed lines indicate hydrogen bonds.

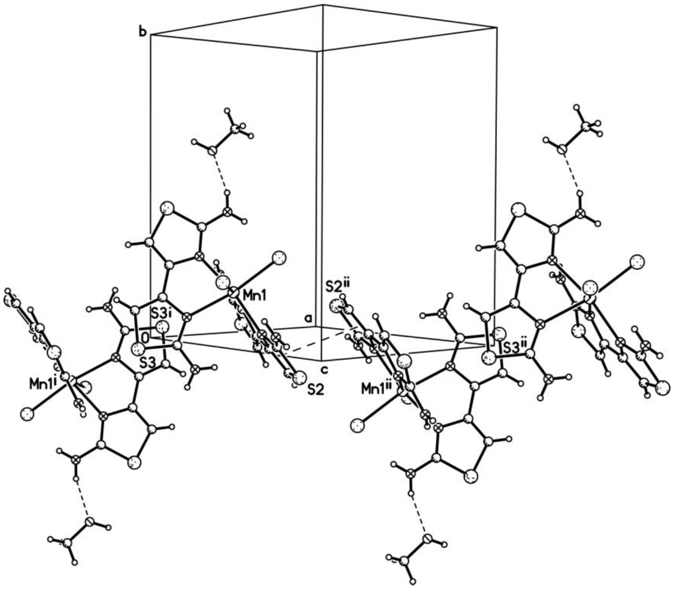


Figure 2
A diagram showing the π–π stacking (dashed line) between thiazole rings. [Symmetry codes: (i) $-x, -y, -z$; (ii) $1 - x, -y, 1 - z$]

In the crystal structure, each complex molecule is hydrogen bonded through N—H···Cl interactions to four neighbouring molecules to form a two-dimensional motif parallel to the (011) plane. The hydrogen-bonded layer is further stabilized by additional hydrogen bonds of the hydroxy groups in the methanol molecules with the amino groups and Cl atoms in the complexes. The thickness of a single layer is 9.713 (12) Å, and the distance between two adjacent layers is 10.867 (6) Å.

The positions of the two dithiazole rings in a hydrogen-bonded layer are different. Those containing S3 and S4 are embedded in the layer, whereas those containing S1 and S2 are on the surface (Fig. 2), which results in the different contributions of the two DABT ligands to the formation of the crystal structure. The S3- and S3^{i}-thiazole rings [symmetry codes as in Fig. 2] are displaced parallel to each other, so that the S atom of one ring lies almost over the centre of the other ring, but the separation of 3.603 (3) Å (for S3^{i}) hardly indicates π–π stacking between them. However, a significant π–π interaction is observed between the S2- and S2^{ii}-thiazole rings, with a smaller separation of 3.422 (3) Å (for S2^{ii}), which dominates the interactions between layers and holds them together to create a three-dimensional supramolecular structure.

Experimental

The DABT ligand was synthesized using the reported method (Erlenmeyer, 1948). $MnCl_2·4H_2O$ (0.050 g, 0.25 mmol) and DABT (0.099 g, 0.5 mmol) were dissolved in methanol (15 ml). The solution was refluxed for 1 h and filtered. The filtrate was kept at room temperature and yellow crystals of a suitable size were obtained after 4 d. Analysis calculated for $C_{13}H_{16}Cl_2MnN_8OS_4$: C 28.16, H 2.91, N 20.21%; found: C 28.85, H 2.87, N 20.59%.

Crystal data

$[MnCl_2(C_6H_6N_4S_2)_2]·CH_4O$
$M_r = 554.42$
Monoclinic, $P2_1/c$
$a = 11.451$ (2) Å
$b = 13.614$ (3) Å
$c = 14.892$ (3) Å
$\beta = 108.39$ (3)°
$V = 2203.0$ (9) Å^3
$Z = 4$
$D_x = 1.672$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.24$ mm^{-1}
$T = 296$ (2) K
Prism, yellow
0.26 × 0.10 × 0.08 mm

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.738$, $T_{max} = 0.907$
16004 measured reflections
3992 independent reflections
3543 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 25.2°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.136$
$S = 1.14$
3992 reflections
263 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0542P)^2 + 3.4155P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.74$ e Å^{-3}
$\Delta\rho_{min} = -0.50$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—Cl1	2.5378 (14)	Mn1—N2	2.247 (3)
Mn1—Cl2	2.5239 (14)	Mn1—N5	2.347 (3)
Mn1—N1	2.259 (4)	Mn1—N6	2.253 (3)

N1—Mn1—N2	74.07 (14)	N2—Mn1—Cl2	93.34 (10)
N1—Mn1—N5	84.68 (13)	N5—Mn1—N6	73.87 (13)
N1—Mn1—N6	98.62 (14)	N5—Mn1—Cl1	90.81 (9)
N1—Mn1—Cl1	170.06 (11)	N5—Mn1—Cl2	168.73 (9)
N1—Mn1—Cl2	92.41 (10)	N6—Mn1—Cl1	88.59 (10)
N2—Mn1—N5	96.31 (12)	N6—Mn1—Cl2	95.88 (10)
N2—Mn1—N6	168.48 (13)	Cl1—Mn1—Cl2	93.66 (5)
N2—Mn1—Cl1	97.71 (10)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$Cl1$^{\rm iii}$	0.82	2.38	3.197 (4)	175
N3—H3$A\cdots$N6	0.86	2.48	3.233 (6)	146
N3—H3$B\cdots$Cl2$^{\rm iv}$	0.86	2.42	3.277 (4)	173
N4—H4$A\cdots$Cl1	0.86	2.44	3.263 (4)	160
N4—H4$B\cdots$O1$^{\rm v}$	0.86	2.36	3.152 (6)	154
N7—H7$A\cdots$N2	0.86	2.60	3.369 (5)	150
N7—H7$B\cdots$Cl1$^{\rm vi}$	0.86	2.52	3.364 (4)	168
N8—H8$A\cdots$Cl2	0.86	2.35	3.144 (4)	154
N8—H8$B\cdots$O1	0.86	2.10	2.915 (6)	159

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

All H atoms were placed in calculated positions, with C—H distances of 0.93 Å (aromatic) or 0.96 Å (CH_3), N—H distances of 0.86 Å, and an O—H distance of 0.82 Å, and were included in the final cycles of refinement as riding, with $U_{\rm iso}$(H) values of 1.2$U_{\rm eq}$(carrier atoms) or 1.5$U_{\rm eq}$(methyl C and hydroxy O).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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