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Bis[bis(benzimidazol-2-ylmethyl)amine]-$\kappa^3N,N',N'';\kappa^2N,N'$-chloromanganese(II) chloride methanol trisolvate

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In the title compound, $[MnClL_2]Cl\cdot3CH_4O$, where L = bis(benzimidazol-2-ylmethyl)amine ($C_{16}H_{15}N_5$), the coordination geometry around the manganese(II) ion can be described as distorted octahedral, involving three benzimidazole N atoms, two tertiary amine atoms and a chloride anion. π–π Stacking interactions are found in two neighboring non-coordinated benzimidazole groups.

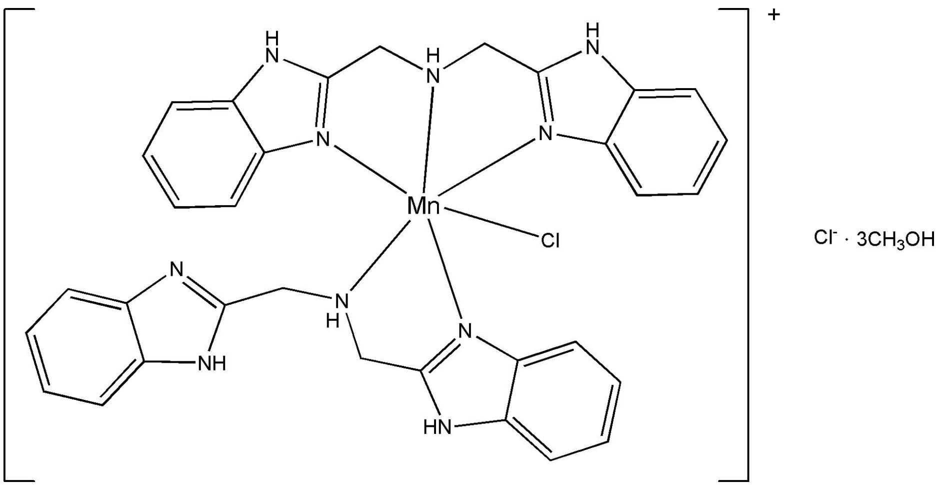
Key indicators

Single-crystal X-ray study
T = 203 K
Mean σ(C–C) = 0.006 Å
R factor = 0.049
wR factor = 0.071
Data-to-parameter ratio = 14.0

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

Comment

The imidazole of the histidine unit is one of the most common binding sites in metalloenzymes, such as alkaline phosphatase and superoxide dismutase (SOD). To understand the chemistry of the assembly and catalytic mechanisms of these metalloenzymes it is logical to prepare potential model compounds by utilizing ligands incorporating the imidazole group. Thus the title Mn^{II} complex, (I), with bis(benzimidazol-2-ylmethyl)amine (L) has been synthesized and its crystal structure is presented here.



(I)

The crystal structure of (I) consists of Mn^{II} complex cations, chloride anions and methanol solvent molecules. The structure of the Mn^{II} complex cation is depicted in Fig. 1. The Mn^{II} ion is surrounded by two L ligands and a chloride anion. One L ligand acts in a tridentate manner and the other acts in a bidentate manner. One chloride anion coordinates to the Mn^{II} ion to complete the distorted octahedral geometry. This structure is similar to that observed in another Mn^{II} complex (Liao *et al.*, 2001). The $Mn—N_{imidazole}$ bond lengths are shorter than the $Mn—N_{imino}$ bonds (Table 1), in agreement with values reported previously (Yan *et al.*, 2004). The Mn—Cl2 bond distance is also comparable to those reported for related

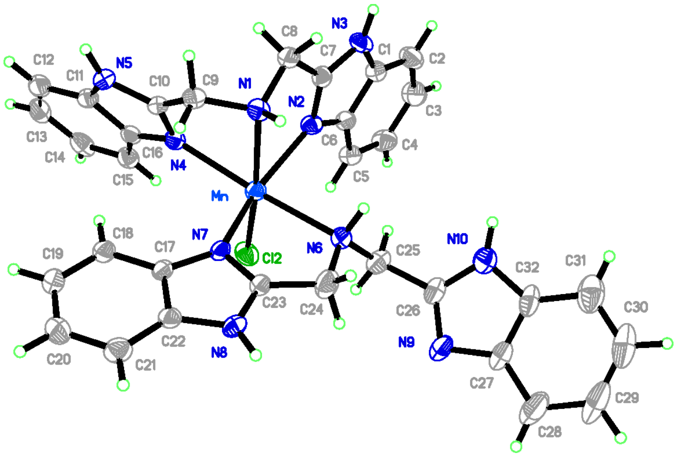


Figure 1
The structure of the cation of (I), with 30% probability displacement ellipsoids (arbitrary spheres for H atoms).

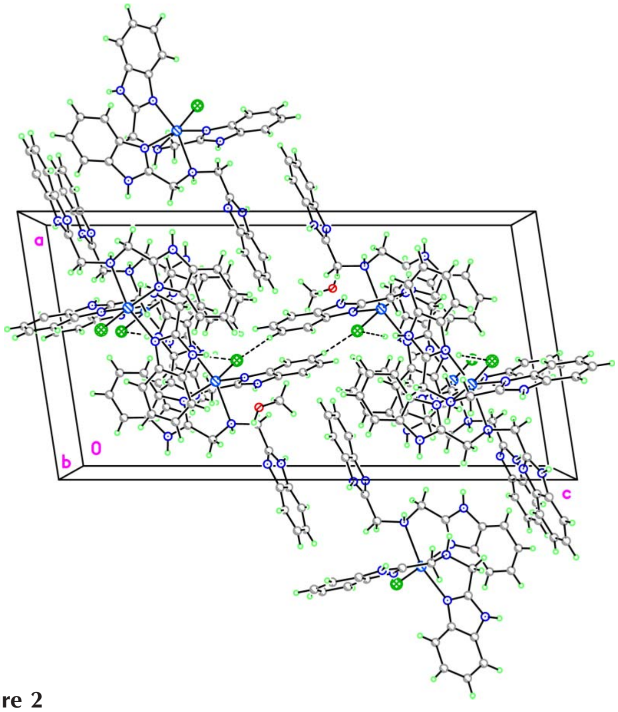


Figure 2
The packing of (I), showing the hydrogen bonding (dashed lines).

structures [2.316 (2)–2.538 (2) Å; Oki *et al.*, 1995]. The benzimidazole rings are planar, the maximum atomic deviation from the least-squares plane being less than 0.02 Å.

There is extensive hydrogen bonding in the crystal structure of (I) (Table 2). Neighboring uncoordinated benzimidazole groups, related by an inversion center, are parallel in an offset fashion and separated by a face-to-face distance of 3.500 (6) Å. This fact indicates the existence of π–π stacking interactions, which stabilize the crystal packing together with the hydrogen-bonding interactions.

Experimental

All chemicals were of reagent grade and commercially available and were used without further purification. Bis(benzimidazol-2-ylmethyl)amine (*L*) was prepared by a previously reported method (Berends & Stephan, 1984). Ligand *L* (2.0 mmol) and $MnCl_2\cdot 4H_2O$ (1.0 mmol) were dissolved in a methanol solution at room temperature. Single crystals of (I) were obtained after three weeks. The elemental analysis agrees with the chemical composition of (I).

Crystal data

$[MnCl(C_{16}H_{15}N_5)_2]Cl\cdot 3CH_4O$
$M_r = 776.63$
Monoclinic, $P2_1/c$
$a = 13.161$ (3) Å
$b = 11.905$ (3) Å
$c = 25.144$ (7) Å
$\beta = 98.794$ (4)°
$V = 3893.2$ (17) Å^3
$Z = 4$
$D_x = 1.325$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2271 reflections
$\theta = 2.3$–20.7°
$\mu = 0.52$ mm^{-1}
$T = 203$ (2) K
Block, colorless
0.40 × 0.30 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{min} = 0.818$, $T_{max} = 0.950$
15680 measured reflections
6860 independent reflections
3596 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$
$\theta_{max} = 25.0°$
$h = -15 \rightarrow 7$
$k = -14 \rightarrow 14$
$l = -29 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.071$
$S = 0.93$
6860 reflections
490 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0102P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn—Cl2	2.425 (1)	Mn—N4	2.202 (2)
Mn—N1	2.444 (3)	Mn—N6	2.389 (3)
Mn—N2	2.187 (3)	Mn—N7	2.204 (3)
N2—Mn—N4	95.50 (9)	N7—Mn—Cl2	99.22 (7)
N2—Mn—N7	154.4 (1)	N6—Mn—Cl2	96.06 (8)
N4—Mn—N7	94.9 (1)	N2—Mn—N1	74.1 (1)
N2—Mn—N6	88.7 (1)	N4—Mn—N1	72.5 (1)
N4—Mn—N6	161.39 (11)	N7—Mn—N1	86.9 (1)
N7—Mn—N6	74.5 (1)	N6—Mn—N1	91.4 (1)
N2—Mn—Cl2	101.73 (8)	Cl2—Mn—N1	171.39 (8)
N4—Mn—Cl2	100.79 (8)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2	0.82	1.82	2.627 (4)	167
O2—H2*A*···N9	0.82	1.93	2.698 (4)	155
O3—H3*A*···Cl1^{i}	0.82	2.34	3.114 (4)	158
N1—H1N···Cl1^{i}	0.93 (2)	2.54 (2)	3.247 (3)	133 (2)
N3—H3N···O1^{ii}	0.89 (1)	1.88 (1)	2.724 (4)	158 (3)
N5—H5N···Cl2^{i}	0.90 (1)	2.26 (1)	3.155 (3)	171 (3)
N6—H6N···Cl1^{i}	0.92 (3)	2.41 (3)	3.292 (3)	161 (3)
N8—H8N···Cl1^{iii}	0.89 (1)	2.21 (1)	3.096 (3)	178 (3)
N10—H10N···O3	0.90 (1)	1.91 (2)	2.754 (4)	156 (3)
C4—H4···Cl2^{iv}	0.93	2.67	3.603 (4)	174

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x, y+1, z$; (iii) $x+1, y, z$; (iv) $-x+1, -y+1, -z+1$.

The hydroxy H atoms and methyl H atoms were placed in calculated positions, with O—H = 0.82 and C—H = 0.96 Å, and refined as rigid groups rotated to fit the electron density, with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(carrier). H atoms on N atoms were located in a difference Fourier map and isotropically refined. Other H atoms were placed in geometrically idealized positions, with C—H = 0.93 Å (aromatic) or 0.97 Å (methylene), and refined as riding with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(carrier).

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

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