A novel bridged asymmetric binuclear manganese(II) complex with DTPB [DTPB is 1,1,4,7,7-pentakis(1H-benzimidazol-2-ylmethyl)-1,4,7-triazaheptane]

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The crystal structure of the title compound, tetrachloro[μ-1,1,4,7,7-pentakis(1H-benzimidazol-2-ylmethyl)-1,4,7-triazaheptane]dimanganese(II) methanol pentasolvate tetrahydrate, $[Mn_2Cl_4(C_{44}H_{43}N_{13})]\cdot 5CH_4O\cdot 4H_2O$, contains an asymmetric dinuclear Mn^{II}–DTPB [DTPB is 1,1,4,7,7-pentakis-(1H-benzimidazol-2-ylmethyl)-1,4,7-triazaheptane] complex with an intra-ligand bridging group ($-NCH_2CH_2N-$), as well as several solvate molecules (methanol and water). Both Mn^{II} cations have similar distorted octahedral coordination geometries. One Mn^{II} cation is coordinated by a Cl^- anion and five N atoms from the ligand, and the other is coordinated by three Cl^- anions and three N atoms of the same ligand. The

$Mn\cdots Mn$ distance is 7.94 Å. A $Cl\cdots H-O\cdots H-O\cdots H-N$ hydrogen-bond chain is also observed, connecting the two parts of the complex.

Comment

In recent years, multinuclear metal complexes containing multi-benzimidazole have attracted much attention in relation to the superoxide dismutase (SOD) enzyme and nuclease mimics (Liao *et al.*, 2001; Liu *et al.*, 2004). Previous research has showed that some DTPB–metal complexes [DTPB is 1,1,4,7,7-pentakis(1H-benzimidazol-2-ylmethyl)-1,4,7-triaza-heptane] can cleave DNA by a hydrolytic mechanism (Liu *et al.*, 2002). Although the DTPB ligand was first synthesized at a very early date, only the complex $Zn_2(DTPB)Cl_4\cdot 3H_2O$ has been crystallographically characterized to date (Birker *et al.*, 1981). As a result of the current interest in DTPB–metal complexes, we have crystallized the title Mn^{II}–DTPB complex, (I), and report its crystal structure here.
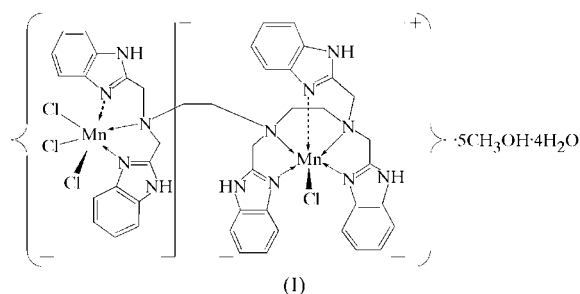
The geometric parameters of (I) are listed in Table 1 and the molecular conformation is illustrated in Fig. 1. The compound contains an asymmetric dinuclear Mn^{II}–DTPB complex with an intra-ligand bridging group ($-NCH_2CH_2N-$), as well as several solvate molecules (methanol and water). In the asymmetric dinuclear complex, both Mn^{II} cations have similar distorted octahedral coordination geometries. Atom Mn1 is
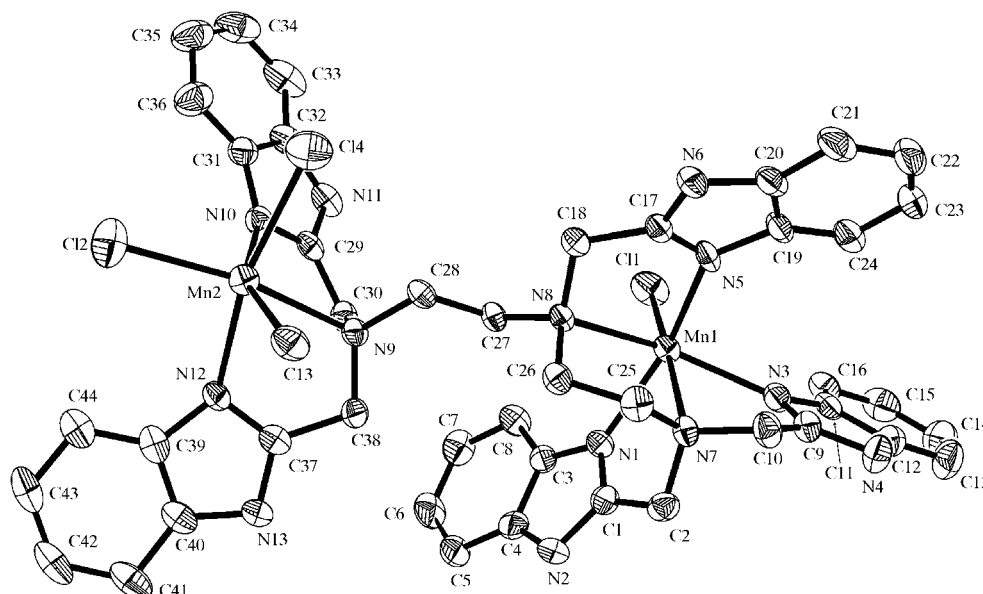

Figure 1
The structure of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

coordinated by a Cl⁻ anion and by five N atoms from three benzimidazole groups and two aliphatic amine groups of the DTPB ligand, leading to a positive charge at the Mn1 coordination moiety. Atom Mn2 is coordinated by three Cl⁻ anions and by three N atoms from the remaining two benzimidazole groups and an aliphatic amine group, giving rise to a negative charge at the Mn2 coordination moiety. Therefore, the whole complex is polar. This is somewhat different from what is seen for $Zn_2(DTPB)Cl_4·3H_2O$, in which the two Zn^{II} atoms have different coordination geometries, one being five-coordinated and the other six-coordinated, resulting in a cationic complex (Birker *et al.*, 1981).

The Mn—N distances in (I) vary considerably. The Mn—N bonds between Mn^{II} cations and aliphatic amine groups range from 2.416 (4) to 2.472 (4) Å, significantly longer than the Mn—N bonds between Mn^{II} cations and benzimidazole groups, with bond lengths ranging from 2.209 (4) to 2.293 (4) Å. The Mn—Cl bonds towards the apical positions in both octahedra are approximately the same [2.397 (2) and 2.423 (2) Å]. However, in the equatorial plane of the Mn2 octahedron, the two Mn—Cl bonds differ, with lengths of 2.471 (2) and 2.660 (2) Å. All these differences are probably the result of the steric requirements for coordination between the ligand and the two Mn^{II} cations. The Mn···Mn distance is 7.94 Å.

The hydrogen-bonding geometry in (I) is listed in Table 2 and illustrated in Fig. 2. The crystal structure of (I) is stabilized by numerous N—H···O, O—H···Cl and O—H···O hydrogen bonds. Each complex links indirectly to neighbouring complexes *via* Cl2···H—O2^i···H—N11^i, Cl3···H—O7^{ii}···H—N13^{iii} and Cl4···H—O4^{iv}···H—N2^{iii} hydrogen

bonds involving methanol or water molecules [symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $1 - x, -y, 1 - z$; (iii) $1 - x, -y, -z$; (iv) $1 - x, 1 - y, 1 - z$]. The hydrogen bonds focus mainly on the Mn2 coordination moiety relative to the Mn1 coordination moiety. It is worth mentioning that a Cl4···H—O1···H—O6^v···H—N6 hydrogen-bond chain is observed, connecting the two parts of complex (I) [symmetry code: (v) $x, y - 1, z$]. Therefore, complex (I) is not only bridged by an intra-ligand group (–NCH₂CH₂N–), but also by this hydrogen-bond chain, forming a large ring of 14 atoms and making the complex more stable.

Experimental

All chemicals were of reagent grade and commercially available from the Beijing Chemical Reagents Company of China; they were used without further purification. DTPB was synthesized by refluxing diethylenetriaminepentaacetic acid and 1,2-diaminobenzene in a 1:5 molar ratio in glycol for 30 h, followed by precipitation of the crude product with water and purification by recrystallization from hot absolute ethanol. DTPB (0.1 mmol) was dissolved in methanol (8 ml) and $MnCl_2$ (0.2 mmol) was dissolved in water (2 ml). The two solutions were mixed and stirred for 30 min at room temperature. After filtration, the filtrate was left at room temperature and crystals of (I) appeared after three months as a result of slow evaporation of the mixed solvent.

Crystal data

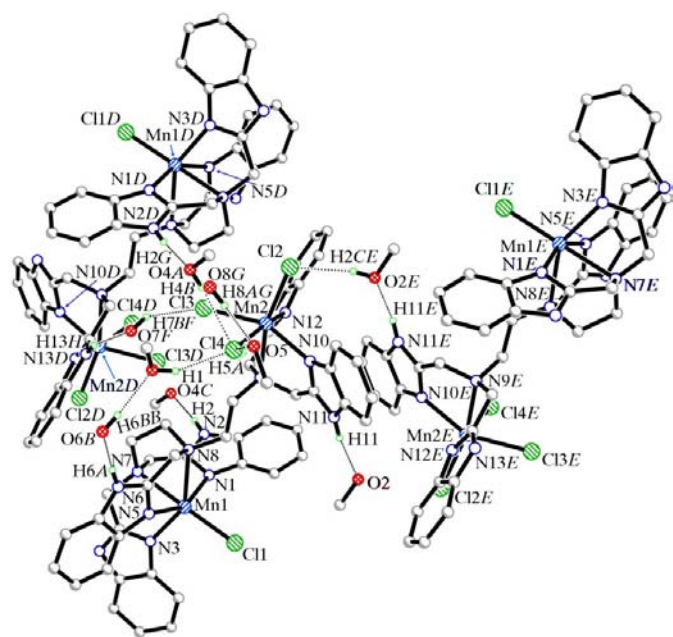|	
$[Mn_2Cl_4(C_{44}H_{43}N_{13})]·5CH_4O·4H_2O$	$Z = 2$
$M_r = 1237.87$	$D_x = 1.372$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 14.254$ (3) Å	Cell parameters from 3090
$b = 15.173$ (3) Å	reflections
$c = 15.852$ (3) Å	$\theta = 2.2–27.1°$
$\alpha = 72.882$ (3)°	$\mu = 0.66$ mm^{-1}
$\beta = 67.976$ (2)°	$T = 183$ (2) K
$\gamma = 75.191$ (3)°	Block, light yellow
$V = 2996.5$ (10) Å^3	$0.30 \times 0.30 \times 0.20$ mm

Figure 2
The hydrogen-bond network in (I). Atoms labelled with the suffixes *A*, *B*, *C*, *D*, *E*, *F* and *G* are at the symmetry positions $(1 - x, 1 - y, 1 - z)$, $(x, y - 1, z)$, $(x, y - 1, z - 1)$, $(1 - x, -y, -z)$, $(1 - x, 1 - y, -z)$, $(1 - x, -y, 1 - z)$ and $(x - 1, y, z)$, respectively.

Table 1
Selected geometric parameters (Å, °).

Mn1—N1	2.209 (4)	Mn2—N10	2.195 (4)
Mn1—N3	2.217 (4)	Mn2—N12	2.293 (4)
Mn1—N5	2.241 (4)	Mn2—Cl2	2.4231 (17)
Mn1—Cl1	2.3972 (16)	Mn2—N9	2.450 (4)
Mn1—N7	2.416 (4)	Mn2—Cl3	2.4710 (16)
Mn1—N8	2.472 (4)	Mn2—Cl4	2.6604 (19)
N1—Mn1—N3	100.34 (16)	N10—Mn2—N12	99.01 (15)
N1—Mn1—N5	152.36 (15)	N10—Mn2—Cl2	98.56 (12)
N3—Mn1—N5	92.41 (15)	N12—Mn2—Cl2	95.94 (12)
N1—Mn1—Cl1	98.83 (12)	N10—Mn2—N9	73.46 (15)
N3—Mn1—Cl1	105.20 (12)	N12—Mn2—N9	70.17 (14)
N5—Mn1—Cl1	101.34 (12)	Cl2—Mn2—N9	162.09 (10)
N1—Mn1—N7	75.06 (14)	N10—Mn2—Cl3	154.63 (12)
N3—Mn1—N7	71.96 (15)	N12—Mn2—Cl3	89.55 (11)
N5—Mn1—N7	85.94 (15)	Cl2—Mn2—Cl3	104.28 (6)
Cl1—Mn1—N7	172.38 (11)	N9—Mn2—Cl3	87.33 (10)
N1—Mn1—N8	82.27 (14)	N10—Mn2—Cl4	81.38 (12)
N3—Mn1—N8	145.44 (15)	N12—Mn2—Cl4	167.53 (12)
N5—Mn1—N8	73.55 (14)	Cl2—Mn2—Cl4	96.32 (6)
Cl1—Mn1—N8	108.44 (11)	N9—Mn2—Cl4	98.23 (10)
N7—Mn1—N8	75.60 (13)	Cl3—Mn2—Cl4	85.25 (5)
Mn1—N8—C27—C28	−177.2 (3)	N8—C27—C28—N9	−145.3 (4)
Mn2—N9—C28—C27	−178.4 (4)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O7—H7$B\cdots$Cl3[i]	0.82	2.44	3.163 (5)	148
O6—H6$B\cdots$O1[ii]	0.82	2.02	2.819 (7)	166
O5—H5$A\cdots$Cl4	0.82	2.23	3.053 (8)	177
O4—H4$\cdots$Cl4[iii]	0.82	2.50	3.240 (5)	152
O2—H2$C\cdots$Cl2[iv]	0.82	2.39	3.134 (6)	152
O1—H1$\cdots$Cl4	0.82	2.33	3.101 (5)	157
N13—H13$A\cdots$O7[v]	0.86	1.93	2.737 (7)	156
N11—H11$\cdots$O2	0.86	1.90	2.749 (7)	171
N6—H6$A\cdots$O6[vi]	0.86	1.93	2.786 (6)	176
N4—H4$A\cdots$O3[vi]	0.86	2.06	2.808 (8)	146
N2—H2$\cdots$O4[vii]	0.86	1.93	2.788 (7)	175
O8—H8$A\cdots$O5[viii]	0.82	2.47	3.225 (17)	154

Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $x, 1+y, z$; (iii) $1-x, 1-y, 1-z$; (iv) $1-x, 1-y, -z$; (v) $x, y, z-1$; (vi) $x, y-1, z$; (vii) $x, y-1, z-1$; (viii) $1+x, y, z$.

Data collection

Bruker SMART 1K CCD area-detector diffractometer	10 238 independent reflections
φ and ω scans	6528 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan ($SADABS$; Sheldrick, 1997)	$R_{int} = 0.033$
$T_{min} = 0.826$, $T_{max} = 0.879$	$\theta_{max} = 25.0°$
12 285 measured reflections	$h = -16 \rightarrow 16$
	$k = -16 \rightarrow 18$
	$l = -11 \rightarrow 18$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.075$	$w = 1/[\sigma^2(F_o^2) + (0.1017P)^2]$
$wR(F^2) = 0.199$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} < 0.001$
10 238 reflections	$\Delta\rho_{max} = 1.23$ e Å^{-3}
704 parameters	$\Delta\rho_{min} = -0.93$ e Å^{-3}

H atoms attached to C, N and methanol O atoms were placed in geometrically idealized positions, with Csp^3—H = 0.97 Å (0.96 Å for methanol), Csp^2—H = 0.93 Å, Nsp^2—H = 0.86 Å and Osp^3—H = 0.82 Å, and constrained to ride on their parent atoms, with U_{iso}(H) = $1.2U_{eq}$(parent atom) [$1.5U_{eq}$(C) for methanol]. H atoms attached to water O atoms were located from difference Fourier maps and their global U_{iso} values were refined. The O—H distances are in the range 0.814–0.824 Å. After several cycles, these H atoms were constrained to ride on their parent atoms, with U_{iso}(H) = $1.2U_{eq}$(O).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

References

Birker, P. J. M. W. L., Schierbeek, A. J., Verschoor, G. C. & Reedijk, J. (1981). *J. Chem. Soc. Chem. Commun.* pp. 1124–1125.
Bruker (2000). *SMART* (Version 5.0) and *SAINT* (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.
Liao, Z.-R., Zheng, X.-F., Luo, B.-S., Shen, L.-R., Li, D.-F., Liu, H.-L. & Zhao, W. (2001). *Polyhedron*, **20**, 2813–2821.
Liu, C.-L., Wang, M., Zhang, T.-L. & Sun, H.-Z. (2004). *Coord. Chem. Rev.* **248**, 147–168.
Liu, C.-L., Yu, S.-W., Li, D.-F., Liao, Z.-R., Sun, X.-H. & Xu, H.-B. (2002). *Inorg. Chem.* **41**, 913–922.
Sheldrick, G. M. (1997). *SHELXS*97, *SHELXL*97 and *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1999). *SHELXTL/PC*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.