

Zi-Lu Chen,* Shi-Bing Li,
Zhi-Hui Qiu, Qing-Fen Zeng and
Fu-Pei LiangCollege of Chemistry and Chemical Engineering,
Guangxi Normal University, Yucui Road 15,
Guilin 541004, People's Republic of ChinaCorrespondence e-mail:
chenziluczl@yahoo.co.uk

Key indicators

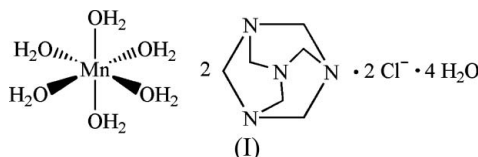
Single-crystal X-ray study
 $T = 294\text{ K}$
Mean $\sigma(\text{Mn}-\text{O}) = 0.002\text{ \AA}$
 R factor = 0.042
 wR factor = 0.111
Data-to-parameter ratio = 18.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Hexaaquamanganese(II) dichloride bis(hexa-
methylenetetramine) tetrahydrate

In the title compound, $[\text{Mn}(\text{H}_2\text{O})_6]\text{Cl}_2 \cdot 2\text{C}_6\text{H}_{12}\text{N}_4 \cdot 4\text{H}_2\text{O}$, each Mn^{II} atom, located on a centre of symmetry, is coordinated by six water molecules in a distorted octahedral coordination geometry. The hexamethylenetetramine (HMTA) molecule does not coordinate to the Mn atom but links with the Mn complex *via* three $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds. The remaining N atom of the HMTA is hydrogen-bonded to the solvent water molecule.

Received 18 August 2005
Accepted 2 September 2005
Online 14 September 2005

Comment

Hexamethylenetetramine (HMTA) has attracted attention because of the desire to construct new supramolecular architectures *via* hydrogen bonding (Carlucci *et al.*, 1995; Ermer & Eling, 1994; Chopra *et al.*, 2005). In order to investigate in detail the contribution of HMTA to the formation of hydrogen bonds, we report here the crystal structure of the title compound, (I).



The crystal structure of (I) is shown in Fig. 1. The crystal of (I) consists of the Mn^{II} complex cations, Cl^- anions, solvent water and uncoordinated HMTA molecules. The Mn^{II} atom is located on an inversion centre and is coordinated by six water molecules in a distorted octahedral geometry (Table 1). The

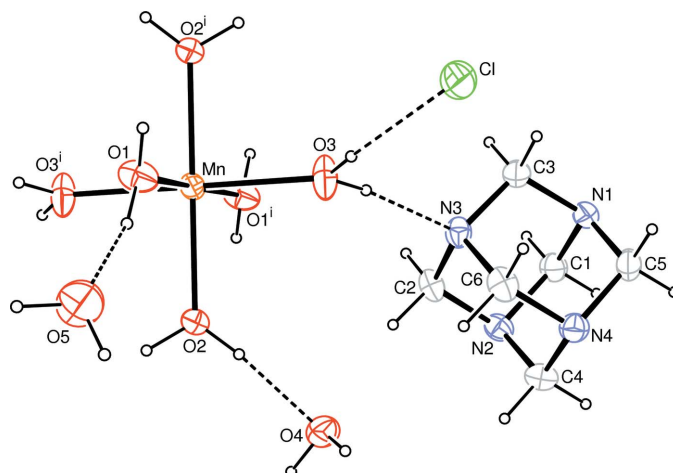


Figure 1

The molecular structure of (I), with 30% probability displacement ellipsoids. Dashed lines indicate hydrogen bonds. Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

HMTA molecule is linked to the Mn^{II} complex cation *via* three O—H···N hydrogen bonds, while atom N4 of HMTA is hydrogen-bonded to the solvent water molecule. The Cl⁻ anions link to the Mn^{II} complex cation *via* O—H···Cl hydrogen bonding (Table 2).

Experimental

An acetonitrile solution (12 ml) of MnCl₂·4H₂O (0.020 g, 3 mmol) and HMTA (0.042 g, 3 mmol) was transferred into a 23 ml Teflon-lined autoclave and heated at 358 K for 72 h. The autoclave was then cooled over a period of 12 h and the solution was filtered. Pale-yellow single crystals of (I) were obtained from the filtrate after 2 d. Elemental analysis for C₁₂H₄₄Cl₂MnN₈O₁₀, calculated: C 24.50, H 7.71, N 18.64%; found: C 24.78, H 7.51, N 18.72%.

Crystal data

[Mn(H ₂ O) ₆]Cl ₂ ·2C ₆ H ₁₂ N ₄ ·4H ₂ O	Z = 1
M _r = 586.39	D _x = 1.369 Mg m ⁻³
Triclinic, P1̄	Mo Kα radiation
a = 9.337 (3) Å	Cell parameters from 1215 reflections
b = 9.531 (2) Å	θ = 2.3–24.6°
c = 9.538 (2) Å	μ = 0.71 mm ⁻¹
α = 119.477 (4)°	T = 294 (2) K
β = 101.018 (5)°	Block, pale yellow
γ = 94.140 (5)°	0.22 × 0.18 × 0.16 mm
V = 711.5 (3) Å ³	

Data collection

Bruker SMART CCD area-detector diffractometer	2850 independent reflections
φ and ω scans	1975 reflections with I > 2σ(I)
Absorption correction: multi-scan (SADABS; Bruker, 1998)	R _{int} = 0.025
T _{min} = 0.840, T _{max} = 0.893	θ _{max} = 26.4°
4034 measured reflections	h = -11 → 10
	k = -10 → 11
	l = -11 → 8

Refinement

Refinement on F ²	H-atom parameters constrained
R[F ² > 2σ(F ²)] = 0.042	w = 1/[σ ² (F _o ²) + (0.0517P) ²]
wR(F ²) = 0.111	where P = (F _o ² + 2F _c ²)/3
S = 1.04	(Δ/σ) _{max} < 0.001
2850 reflections	Δρ _{max} = 0.28 e Å ⁻³
151 parameters	Δρ _{min} = -0.27 e Å ⁻³

Table 1

Selected bond distances (Å).

Mn—O1	2.1642 (17)	Mn—O3	2.1707 (19)
Mn—O2	2.1421 (18)		

Table 2

Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1C···O5	0.98	1.75	2.717 (4)	167
O1—H1D···N2 ⁱ	0.90	1.92	2.817 (3)	176
O2—H2C···N1 ⁱⁱ	0.89	1.94	2.808 (4)	163
O2—H2D···O4	0.87	1.83	2.700 (3)	173
O3—H3C···Cl	0.83	2.36	3.165 (3)	163
O3—H3D···N3	0.84	1.97	2.800 (4)	173
O4—H4C···Cl ⁱⁱⁱ	0.94	2.25	3.151 (2)	161
O4—H4D···N4 ^{iv}	0.88	1.96	2.827 (3)	168
O5—H5C···Cl ⁱⁱ	0.93	2.30	3.228 (3)	176
O5—H5D···Cl ^v	0.87	2.35	3.205 (3)	170

Symmetry codes: (i) x, y, z - 1; (ii) x, y + 1, z; (iii) x, y + 1, z + 1; (iv) -x + 2, -y + 1, -z + 2; (v) -x + 2, -y + 1, -z + 1.

Water H atoms were located in a difference Fourier map and refined as riding in their as-found positions relative to the O atoms, with U_{iso}(H) = 1.5U_{eq}(O). H atoms on C atoms were placed in calculated positions with C—H = 0.97 Å and refined in riding mode, with U_{iso}(H) = 1.2U_{eq}(C).

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, 1997); software used to prepare material for publication: SHELXTL.

The authors thank the Scientific Research Foundation of Guangxi Normal University and the Science Foundation of Guangxi (Guikeqing 0542021), China.

References

Bruker (1997). SHELXTL. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (1998). SMART (Version 5.051), SAINT (Version 5.01) and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
 Carlucci, L., Ciani, G., Proserpio, D. M. & Sironi, A. (1995). *J. Am. Chem. Soc.* **117**, 12861.
 Chopra, D., Dagur, P., Prakash, A. S., Guru Row, T. N. & Hegde, M. S. (2005). *J. Cryst. Growth*, **275**, e2049–e2053.
 Ermer, O. & Eling, A. (1994). *J. Chem. Soc. Perkin Trans. 2*, pp. 925–944.
 Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.