Diaquabis(hexamethylenetetramine-*N*)bis(isothiocyanato)manganese(II) tetraaquabis(isothiocyanato)-manganese(II) dihydrate

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The crystal structure of the title compound, $[Mn(NCS)_2(hmt)_2(H_2O)_2]\cdot[Mn(NCS)_2(H_2O)_4]\cdot 2H_2O$, where hmt is hexamethylenetetramine ($C_6H_{12}N_4$), shows that each Mn atom is in an octahedral coordination enviroment, and that the independent uncharged components $[Mn(NCS)_2(hmt)_2(H_2O)_2]$, $[Mn(NCS)_2(H_2O)_4]$ and H_2O are linked together by three kinds of hydrogen bonds (O—H···N, O—H···O and O—H···S) to form a three-dimensional supramolecular structure.

Comment

Metal complexes that assemble into specific supramolecular structures in the crystal lattice have generated considerable interest because of their potential use in developing new materials with magnetic, optical and catalytic properties (Lehn, 1990). Materials with multidimensional supramolecular architectures have been organized by coordinate, covalent or hydrogen bonding (Gemma & Jonathan, 1999). The vast majority of current work centers around the controlled assembly of donor and acceptor building blocks (particularly involving hydrogen-bond acid–base pairs, *e.g.* nucleobase) in order to generate an entirely supramolecular polymer, *i.e.* a material held together solely by non-covalent interactions. With this in mind, considering hexamethylenetetramine (hmt) as a potential tetradentate ligand or hydrogen-bond acceptor, and suitable for the self-assembly of supramolecular architectures (Stuart *et al.*, 1998), we sought to synthesize a multidimensional supramolecular compound containing it. Herein we report the three-dimensional supramolecular architecture of $[Mn(hmt)_2(H_2O)_2(NCS)_2]\cdot[Mn(H_2O)_4(NCS)_2]\cdot 2H_2O$, (I).
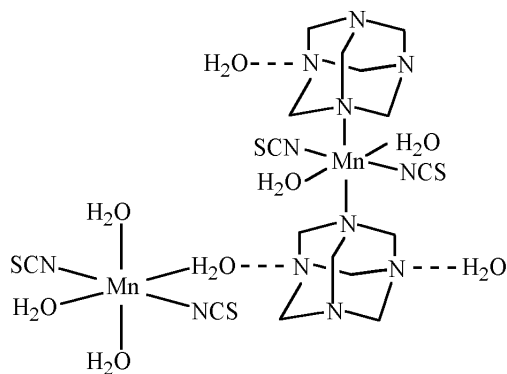
(I)

The molecular structure of (I) is shown in Fig. 1. The geometry around Mn1 is octahedral; the two O atoms of the coordinated water molecules and the two N atoms from two
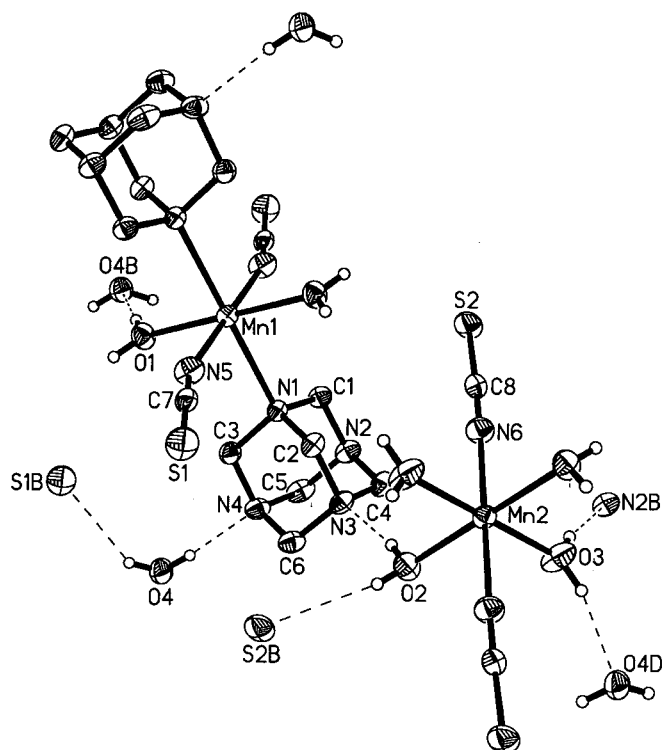
Figure 1
The molecular structure of the title compound showing 40% probability displacement ellipsoids and some neighbouring atoms linked by hydrogen bonds.

NCS⁻ define the equatorial positions, whereas an N atom from each of the hmt ligands occupies the axial ones. The axial Mn1—N1 bond distance of 2.4213 (13) Å is significantly longer than the equatorial Mn1—O1 bonds of 2.1865 (12) Å and the Mn1—N5 bonds of 2.1342 (15) Å. Mn2 is also in an octahedral environment. The coordination polyhedron is formed by two NCS⁻ and four water molecules, elongated along the axis defined by the water molecules; the axial Mn2—O2 distance is 2.2132 (13) Å. Both Mn1 and Mn2 containing species are located on inversion centres. In Fig. 2, both the interlayer Mn1···Mn1 and Mn2···Mn2 distances are 7.969 Å, the distance of Mn1...Mn1 between adjacent chains is 9.280 Å in the same layer, the shortest intermolecular Mn1···Mn2 distance is 7.296 Å and the shorter intermolecular Mn1···Mn2 distance is 8.640 Å. The independent moieties [Mn(hmt)₂-(H₂O)₂(NCS)₂] and [Mn(H₂O)₄(NCS)₂] are connected by four hydrogen bonds (Table 2) to form a two-dimensional structure. Adjacent two-dimensional chains are connected by further hydrogen bonds to form a three-dimensional supramolecular architecture.

Experimental

To 1 mmol of hmt and 2 mmol of $MnCl_2.4H_2O$ in 3.5 ml of water solution, 2 ml aqueous solution of NH_4SCN was added and the mixture stirred for *ca* 10 min. The resulting solution was allowed to stand for 2 d. Colorless crystals were collected in 34% yield.
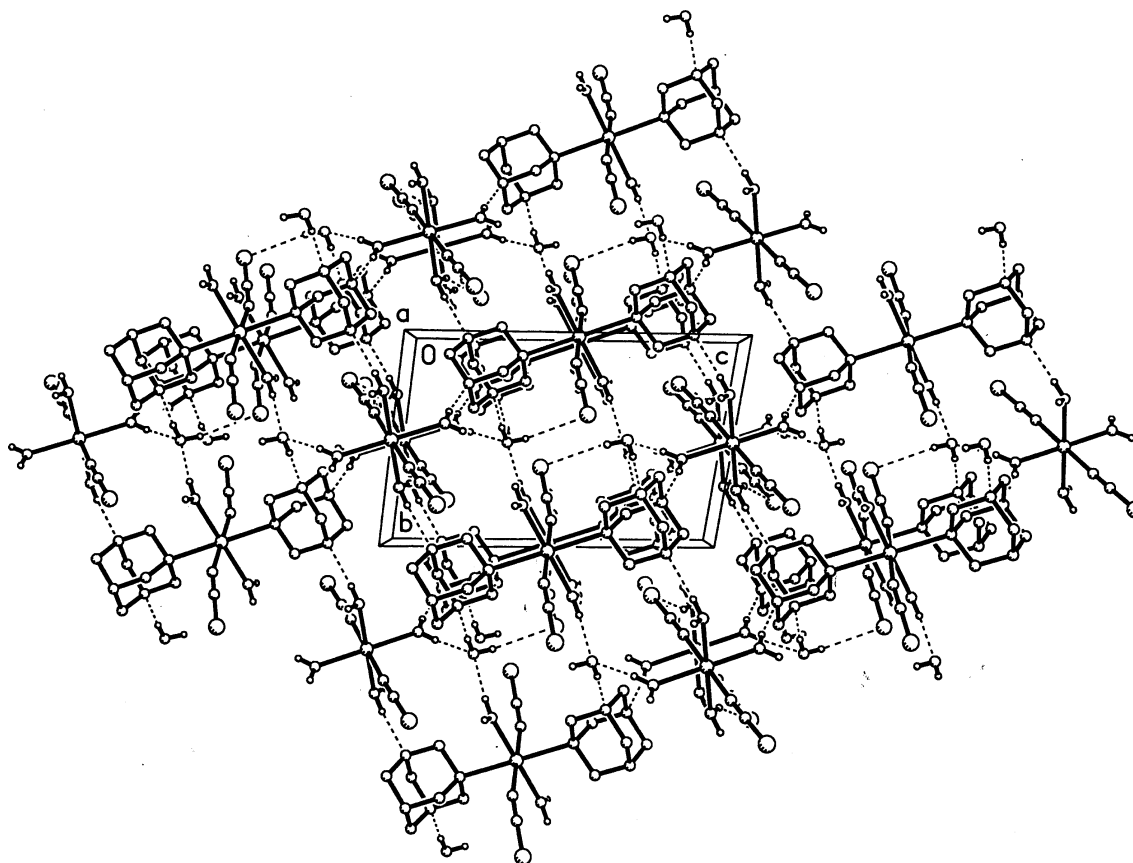

Figure 2
Packing diagram of the title compound, viewed along the *a* axis.

Crystal data

[Mn(NCS)$_2$(C$_6$H$_{12}$N$_4$)$_2$(H$_2$O)$_2$]·-
 [Mn(NCS)$_2$(H$_2$O)$_4$]·2H$_2$O
$M_r = 766.72$
Triclinic, $P\bar{1}$
$a = 7.969\,(1)$ Å
$b = 9.111\,(1)$ Å
$c = 13.076\,(2)$ Å
$\alpha = 94.34\,(1)°$
$\beta = 96.83\,(1)°$
$\gamma = 115.16\,(1)°$
$V = 844.76\,(19)$ Å^3

$Z = 1$
$D_x = 1.507$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 26
 reflections
$\theta = 2.8–17.2°$
$\mu = 1.05$ mm^{-1}
$T = 288\,(2)$ K
Block, colorless
$0.48 \times 0.48 \times 0.40$ mm

Data collection

Siemens $P4$ diffractometer
ω scans
Absorption correction: ψ scan
 (*XSCANS*; Siemens, 1994)
 $T_{min} = 0.615$, $T_{max} = 0.653$
3694 measured reflections
3316 independent reflections
2853 reflections with $I > 2\sigma(I)$

$R_{int} = 0.010$
$\theta_{max} = 26.0°$
$h = 0 \rightarrow 9$
$k = -11 \rightarrow 10$
$l = -16 \rightarrow 16$
3 standard reflections
 every 97 reflections
 intensity decay: 3.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.062$
$S = 1.06$
3316 reflections
226 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2$
 $ + 0.1263P]$
 where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0364 (17)

Table 1
Selected geometric parameters (Å, °).

Mn1—N5	2.1341 (15)	Mn2—O3	2.1616 (13)
Mn1—O1	2.1866 (12)	Mn2—N6	2.1886 (15)
Mn1—N1	2.4213 (13)	Mn2—O2	2.2132 (13)
N5—Mn1—O1	90.22 (6)	O3—Mn2—N6^{ii}	91.79 (6)
N5—Mn1—N1	88.20 (5)	O3—Mn2—O2	90.22 (6)
N5^i—Mn1—N1^i	88.20 (5)	N6—Mn2—O2	91.64 (5)

Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $-x, -1-y, -z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4OB···S1^i	0.818 (5)	2.631 (14)	3.3533 (16)	148 (2)
O2—H2OB···S2^{ii}	0.822 (5)	2.536 (11)	3.2949 (15)	154 (2)
O4—H4OA···N4	0.819 (5)	2.001 (6)	2.817 (2)	174 (3)
O2—H2OA···N3	0.823 (5)	1.992 (7)	2.8055 (19)	170 (2)
O3—H3OB···O4^{iii}	0.816 (5)	1.998 (7)	2.797 (2)	166 (2)
O3—H3OA···N2^{iv}	0.815 (5)	2.040 (7)	2.843 (2)	168.5 (19)
O1—H1OA···O4^v	0.818 (5)	1.925 (6)	2.7424 (19)	176 (2)

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

H atoms were placed in calculated positions (C—H = 0.97 Å), assigned fixed isotropic displacement parameters at 1.2 times the equivalent U_{iso} of the atoms to which they are attached and were allowed to ride on their respective parent atoms.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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