

Bis(acetylacetonato- κ^2O,O')(methanol- κO)(thiocyanato- κN)manganese(III)

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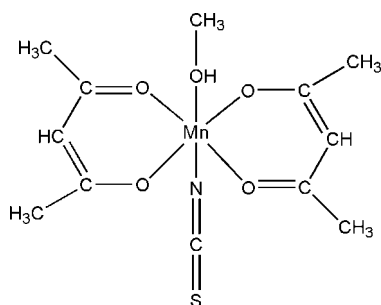
Received 7 September 2008; accepted 30 September 2008

 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.009$ Å; R factor = 0.058; wR factor = 0.148; data-to-parameter ratio = 15.0.

In the title complex, $[Mn(C_5H_7O_2)_2(NCS)(CH_4O)]$, the Mn^{III} atom has a slightly distorted octahedral coordination formed by five O atoms and one N atom. The equatorial positions are occupied by four O atoms of two acetylacetonate ligands, while the axial positions are occupied by the N atom of the thiocyanate anion and the O atom of the methanol molecule. In the crystal structure, complex molecules are linked by an intermolecular O—H...S hydrogen bond, forming a chain running along [101].

Related literature

For the synthesis, see: Stults *et al.* (1975). For related structures, see: Stults *et al.* (1979); Swarnabala *et al.* (1994).



Experimental

Crystal data

 $[Mn(C_5H_7O_2)_2(NCS)(CH_4O)]$
 $M_r = 343.27$

 Monoclinic, $P2_1/n$
 $a = 7.4795$ (13) Å

 $b = 12.420$ (2) Å

 $c = 17.586$ (3) Å

 $\beta = 98.673$ (4)°

 $V = 1614.9$ (5) Å³
 $Z = 4$

 Mo $K\alpha$ radiation

 $\mu = 0.96$ mm⁻¹
 $T = 293$ (2) K

 $0.21 \times 0.19 \times 0.15$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer

 Absorption correction: multi-scan (*SADABS*; Bruker, 2000)

 $T_{\min} = 0.824$, $T_{\max} = 0.869$

7925 measured reflections

2830 independent reflections

 1276 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.112$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.058$
 $wR(F^2) = 0.148$
 $S = 0.91$

2830 reflections

189 parameters

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.33$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.33$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O5-H5A\cdots S1^i$	0.78 (7)	2.51 (6)	3.281 (4)	168 (7)

 Symmetry code: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *SAINT-Plus* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2333).

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supporting information

Acta Cryst. (2008). E64, m1363 [doi:10.1107/S1600536808031589]

Bis(acetylacetonato- κ^2O,O')(methanol- κO)(thiocyanato- κN)manganese(III)**Shuang-Ming Meng, Hai Xie, Yue-Qin Fan and Yong Guo****S1. Comment**

Octahedral complexes of high-spin Mn^{III} are good examples for investigating the Jahn-Teller distortions, because their geometry are always distorted from the ideal octahedron to the distorted one by the axial ligands. Here, we report the structure of an octahedral Mn^{III} complex, whose synthesis has been reported early (Stults *et al.*, 1975).

The molecular structure of the title complex is shown in Figure 1. The Mn^{III} atom is six coordinated by five O atoms and one N atom. The geometry can be described as a distorted octahedron. Four equatorial positions are occupied by four O atoms coming from two acetylacetonate ligands with the average Mn—O bond length 1.909 Å, which is in agreement well with the corresponding distance in [Mn(acac)₂(OH₂)₂]ClO₄·2H₂O. (Swarnabala *et al.*, 1994). One SCN⁻ ion and one methanol molecule are coordinated to the Mn^{III} atom with *trans* positions, so that forming an octahedral geometry. The distance of Mn—O_{methanol} [2.289 (5) Å] is obviously longer than the bond lengths of Mn—O_{acetylacetonate}. The bond length of Mn—N_{SCN} is 2.187 (6) Å, which is also consistent with that found in [Mn(acac)₂(SCN)] (Stults *et al.*, 1979). In the crystal structure, a molecular chain along the [101] direction is formed by an intermolecular H-bond between the O atom of the methanol molecule and the S atom of the SCN⁻ ion (Table 1).

S2. Experimental

The title complex was synthesized according to the literature method (Stults *et al.* 1975). The single crystals suitable for X-ray diffraction were grown from a methanol solution after the solvent was partial evaporated. Anal. Calcd for C₁₂H₁₈MnNO₅S: C 41.99, H 5.29, N 4.08; found: C 42.04, H 5.26, N, 4.11.

S3. Refinement

The O-bound H atom of the methanol molecule was located in a difference Fourier map and its coordinates were refined, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. The H atoms bound to C atoms were placed geometrically (C—H = 0.93–0.96 Å) and were refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$.

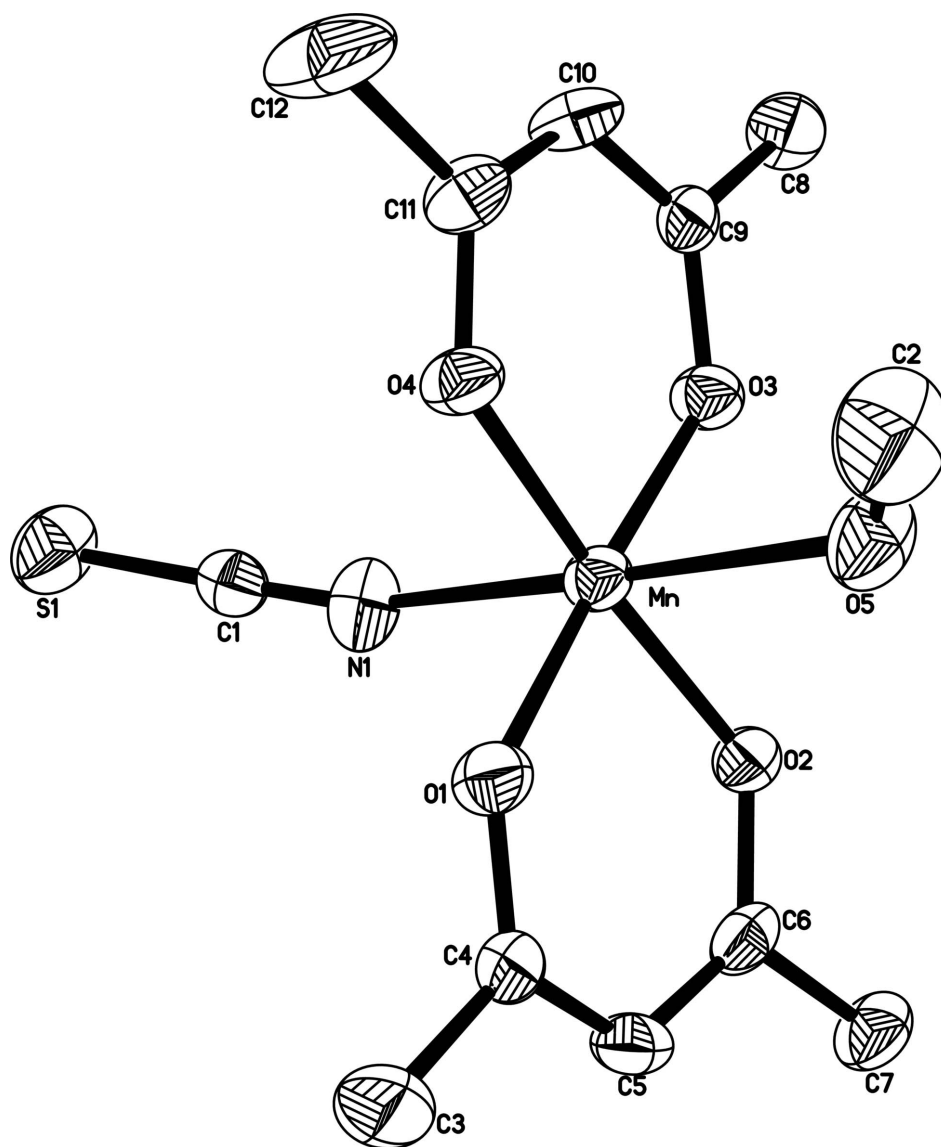


Figure 1

A view of the title complex with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted.

Bis(acetylacetonato- κ^2 O,O')(methanol- κ O)(thiocyanato- κ N)manganese(III)

Crystal data

[Mn(C₅H₇O₂)₂(NCS)(CH₄O)]

$M_r = 343.27$

Monoclinic, $P2_1/n$

Hall symbol: $-P2_1n$

$a = 7.4795$ (13) Å

$b = 12.420$ (2) Å

$c = 17.586$ (3) Å

$\beta = 98.673$ (4)°

$V = 1614.9$ (5) Å³

$Z = 4$

$F(000) = 712$

$D_x = 1.412$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1347 reflections

$\theta = 2.8\text{--}16.2^\circ$

$\mu = 0.96$ mm⁻¹

$T = 293$ K

Block, brown

$0.21 \times 0.19 \times 0.15$ mm

Data collection

Bruker APEXII CCD area-detector
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
 φ and ω scans
Absorption correction: multi-scan
(*SADABS*; Bruker, 2000)
 $T_{\min} = 0.824$, $T_{\max} = 0.869$

7925 measured reflections
2830 independent reflections
1276 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.112$
 $\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 2.0^\circ$
 $h = -8 \rightarrow 8$
 $k = -14 \rightarrow 14$
 $l = -16 \rightarrow 20$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.058$
 $wR(F^2) = 0.148$
 $S = 0.91$
2830 reflections
189 parameters
0 restraints
Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map
H atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0541P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.33 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Mn	0.86466 (12)	0.33696 (7)	0.64488 (5)	0.0398 (3)
S1	1.1860 (3)	0.34036 (15)	0.90976 (10)	0.0749 (7)
O1	1.0806 (5)	0.3054 (3)	0.6035 (2)	0.0504 (12)
O2	0.7813 (5)	0.1923 (3)	0.6275 (2)	0.0446 (11)
O3	0.6418 (5)	0.3674 (3)	0.6806 (2)	0.0458 (11)
O4	0.9347 (5)	0.4844 (3)	0.6515 (2)	0.0485 (12)
O5	0.7201 (7)	0.3709 (4)	0.5230 (3)	0.0682 (16)
H5A	0.701 (11)	0.325 (6)	0.491 (4)	0.102*
C1	1.0772 (9)	0.3201 (5)	0.8239 (4)	0.0455 (17)
C2	0.7403 (12)	0.4605 (6)	0.4764 (4)	0.100 (3)
H2A	0.7848	0.5205	0.5082	0.150*
H2B	0.6253	0.4788	0.4471	0.150*
H2C	0.8245	0.4437	0.4420	0.150*
C3	1.3234 (9)	0.2126 (6)	0.5642 (5)	0.084 (3)
H3A	1.3176	0.2455	0.5144	0.126*
H3B	1.3652	0.1398	0.5620	0.126*
H3C	1.4055	0.2524	0.6011	0.126*

C4	1.1395 (9)	0.2130 (6)	0.5877 (4)	0.0491 (17)
C5	1.0421 (9)	0.1195 (5)	0.5885 (4)	0.0537 (19)
H5	1.0977	0.0559	0.5768	0.064*
C6	0.8682 (10)	0.1122 (5)	0.6054 (3)	0.0472 (18)
C7	0.7645 (9)	0.0081 (4)	0.5966 (4)	0.061 (2)
H7A	0.7050	-0.0029	0.6407	0.091*
H7B	0.8463	-0.0504	0.5924	0.091*
H7C	0.6758	0.0110	0.5511	0.091*
C8	0.4019 (8)	0.4572 (5)	0.7255 (4)	0.058 (2)
H8A	0.3125	0.4324	0.6842	0.088*
H8B	0.3704	0.5280	0.7408	0.088*
H8C	0.4067	0.4089	0.7684	0.088*
C9	0.5827 (8)	0.4605 (5)	0.6990 (3)	0.0415 (16)
C10	0.6804 (9)	0.5539 (5)	0.6967 (4)	0.0531 (19)
H10	0.6281	0.6168	0.7118	0.064*
C11	0.8462 (10)	0.5633 (5)	0.6743 (4)	0.0510 (18)
C12	0.9380 (10)	0.6708 (5)	0.6760 (5)	0.092 (3)
H12A	1.0490	0.6684	0.7114	0.138*
H12B	0.8603	0.7250	0.6922	0.138*
H12C	0.9636	0.6880	0.6255	0.138*
N1	0.9996 (8)	0.3080 (5)	0.7624 (3)	0.0617 (17)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn	0.0393 (6)	0.0339 (5)	0.0471 (6)	-0.0035 (5)	0.0093 (4)	-0.0032 (5)
S1	0.1019 (17)	0.0683 (13)	0.0490 (12)	-0.0013 (13)	-0.0060 (11)	0.0010 (11)
O1	0.043 (3)	0.046 (3)	0.065 (3)	-0.007 (2)	0.017 (2)	-0.012 (2)
O2	0.043 (3)	0.035 (2)	0.055 (3)	-0.003 (2)	0.005 (2)	-0.004 (2)
O3	0.041 (3)	0.041 (2)	0.057 (3)	-0.001 (2)	0.013 (2)	-0.003 (2)
O4	0.052 (3)	0.034 (2)	0.063 (3)	-0.003 (2)	0.016 (2)	-0.005 (2)
O5	0.090 (4)	0.069 (4)	0.043 (3)	-0.006 (3)	0.001 (3)	0.000 (3)
C1	0.041 (4)	0.042 (4)	0.056 (5)	-0.002 (3)	0.015 (4)	0.006 (4)
C2	0.135 (8)	0.097 (7)	0.061 (6)	-0.012 (6)	-0.003 (5)	0.024 (5)
C3	0.052 (5)	0.096 (6)	0.108 (7)	0.002 (4)	0.029 (5)	-0.041 (5)
C4	0.045 (5)	0.057 (4)	0.044 (4)	0.005 (4)	0.001 (3)	-0.013 (4)
C5	0.049 (5)	0.040 (4)	0.073 (5)	0.008 (4)	0.011 (4)	-0.010 (4)
C6	0.064 (5)	0.042 (4)	0.034 (4)	-0.002 (4)	0.001 (4)	-0.007 (3)
C7	0.076 (5)	0.038 (4)	0.066 (5)	-0.009 (4)	0.004 (4)	-0.007 (4)
C8	0.048 (5)	0.072 (5)	0.059 (5)	0.001 (4)	0.022 (4)	-0.014 (4)
C9	0.043 (4)	0.048 (4)	0.031 (4)	0.005 (3)	0.001 (3)	-0.006 (3)
C10	0.073 (6)	0.036 (4)	0.055 (5)	0.001 (4)	0.026 (4)	-0.011 (3)
C11	0.063 (5)	0.042 (4)	0.051 (5)	-0.010 (4)	0.019 (4)	-0.001 (4)
C12	0.109 (7)	0.039 (4)	0.140 (8)	-0.012 (5)	0.061 (6)	-0.015 (5)
N1	0.062 (4)	0.067 (4)	0.054 (4)	-0.015 (3)	0.001 (3)	0.003 (3)

Geometric parameters (Å, °)

Mn—O4	1.903 (4)	C3—H3C	0.9600
Mn—O2	1.911 (4)	C4—C5	1.372 (8)
Mn—O3	1.906 (4)	C5—C6	1.380 (8)
Mn—O1	1.910 (4)	C5—H5	0.9300
Mn—N1	2.189 (6)	C6—C7	1.505 (8)
Mn—O5	2.289 (5)	C7—H7A	0.9600
S1—C1	1.623 (8)	C7—H7B	0.9600
O1—C4	1.275 (6)	C7—H7C	0.9600
O2—C6	1.280 (7)	C8—C9	1.495 (8)
O3—C9	1.296 (6)	C8—H8A	0.9600
O4—C11	1.281 (7)	C8—H8B	0.9600
O5—C2	1.405 (8)	C8—H8C	0.9600
O5—H5A	0.80 (7)	C9—C10	1.375 (8)
C1—N1	1.157 (7)	C10—C11	1.361 (8)
C2—H2A	0.9600	C10—H10	0.9300
C2—H2B	0.9600	C11—C12	1.501 (8)
C2—H2C	0.9600	C12—H12A	0.9600
C3—C4	1.494 (8)	C12—H12B	0.9600
C3—H3A	0.9600	C12—H12C	0.9600
C3—H3B	0.9600		
O4—Mn—O2	173.85 (19)	O1—C4—C5	123.9 (6)
O4—Mn—O3	92.02 (17)	O1—C4—C3	115.2 (6)
O2—Mn—O3	87.66 (16)	C5—C4—C3	120.8 (6)
O4—Mn—O1	88.83 (17)	C4—C5—C6	125.2 (6)
O2—Mn—O1	91.17 (17)	C4—C5—H5	117.4
O3—Mn—O1	176.83 (18)	C6—C5—H5	117.4
O4—Mn—N1	91.0 (2)	O2—C6—C5	123.6 (6)
O2—Mn—N1	95.16 (19)	O2—C6—C7	114.9 (6)
O3—Mn—N1	91.32 (19)	C5—C6—C7	121.5 (6)
O1—Mn—N1	91.7 (2)	C6—C7—H7A	109.5
O4—Mn—O5	88.09 (17)	C6—C7—H7B	109.5
O2—Mn—O5	85.76 (18)	H7A—C7—H7B	109.5
O3—Mn—O5	87.65 (18)	C6—C7—H7C	109.5
O1—Mn—O5	89.33 (18)	H7A—C7—H7C	109.5
N1—Mn—O5	178.6 (2)	H7B—C7—H7C	109.5
C4—O1—Mn	127.4 (4)	C9—C8—H8A	109.5
C6—O2—Mn	127.6 (4)	C9—C8—H8B	109.5
C9—O3—Mn	127.4 (4)	H8A—C8—H8B	109.5
C11—O4—Mn	127.2 (4)	C9—C8—H8C	109.5
C2—O5—Mn	128.0 (4)	H8A—C8—H8C	109.5
C2—O5—H5A	100 (6)	H8B—C8—H8C	109.5
Mn—O5—H5A	123 (6)	O3—C9—C10	122.8 (6)
N1—C1—S1	178.5 (7)	O3—C9—C8	114.3 (5)
O5—C2—H2A	109.5	C10—C9—C8	122.9 (6)
H5A—C2—H2A	136.0	C11—C10—C9	126.3 (6)

O5—C2—H2B	109.5	C11—C10—H10	116.8
H5A—C2—H2B	98.6	C9—C10—H10	116.8
H2A—C2—H2B	109.5	O4—C11—C10	124.2 (6)
O5—C2—H2C	109.5	O4—C11—C12	115.5 (6)
H5A—C2—H2C	91.3	C10—C11—C12	120.3 (6)
H2A—C2—H2C	109.5	C11—C12—H12A	109.5
H2B—C2—H2C	109.5	C11—C12—H12B	109.5
C4—C3—H3A	109.5	H12A—C12—H12B	109.5
C4—C3—H3B	109.5	C11—C12—H12C	109.5
H3A—C3—H3B	109.5	H12A—C12—H12C	109.5
C4—C3—H3C	109.5	H12B—C12—H12C	109.5
H3A—C3—H3C	109.5	C1—N1—Mn	162.9 (6)
H3B—C3—H3C	109.5		
O4—Mn—O1—C4	174.8 (5)	Mn—O1—C4—C5	9.1 (9)
O2—Mn—O1—C4	-11.4 (5)	Mn—O1—C4—C3	-173.5 (4)
N1—Mn—O1—C4	83.8 (5)	O1—C4—C5—C6	0.8 (11)
O5—Mn—O1—C4	-97.1 (5)	C3—C4—C5—C6	-176.4 (6)
O3—Mn—O2—C6	-175.2 (5)	Mn—O2—C6—C5	-1.7 (8)
O1—Mn—O2—C6	7.7 (5)	Mn—O2—C6—C7	-179.7 (4)
N1—Mn—O2—C6	-84.2 (5)	C4—C5—C6—O2	-4.7 (10)
O5—Mn—O2—C6	96.9 (5)	C4—C5—C6—C7	173.2 (6)
O4—Mn—O3—C9	0.7 (5)	Mn—O3—C9—C10	-1.7 (8)
O2—Mn—O3—C9	-173.2 (5)	Mn—O3—C9—C8	-179.9 (3)
N1—Mn—O3—C9	91.7 (5)	O3—C9—C10—C11	1.3 (10)
O5—Mn—O3—C9	-87.3 (5)	C8—C9—C10—C11	179.4 (6)
O3—Mn—O4—C11	0.8 (5)	Mn—O4—C11—C10	-1.3 (9)
O1—Mn—O4—C11	177.8 (5)	Mn—O4—C11—C12	177.7 (4)
N1—Mn—O4—C11	-90.5 (5)	C9—C10—C11—O4	0.3 (11)
O5—Mn—O4—C11	88.4 (5)	C9—C10—C11—C12	-178.7 (6)
O4—Mn—O5—C2	15.3 (5)	O4—Mn—N1—C1	5.2 (18)
O3—Mn—O5—C2	107.5 (5)	O3—Mn—N1—C1	-86.9 (18)
O1—Mn—O5—C2	-73.5 (5)	O1—Mn—N1—C1	94.0 (18)
O2—Mn—O5—C2	-164.7 (5)	O2—Mn—N1—C1	-174.6 (18)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5A \cdots S1 ⁱ	0.78 (7)	2.51 (6)	3.281 (4)	168 (7)

Symmetry code: (i) $x-1/2, -y+1/2, z-1/2$.