Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

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

Shuang-Ming Meng,* Hai Xie, Yue-Qin Fan and Yong Guo

College of Chemistry and Chemical Engineering, Shanxi Datong University, Shanxi 037009, People's Republic of China
Correspondence e-mail: xhtgao@126.com

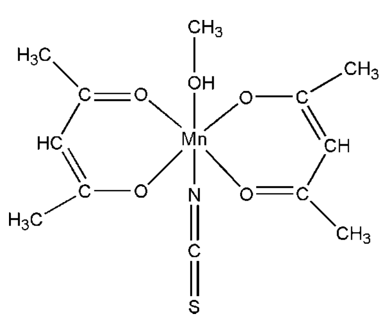
Received 7 September 2008; accepted 30 September 2008

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(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
β = 98.673 (4)°
V = 1614.9 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.96 mm^{-1}
T = 293 (2) K
0.21 × 0.19 × 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_{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
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5A···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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supplementary materials

Acta Cryst. (2008). E**64**, m1363 [**doi:10.1107/S1600536808031589**]

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

S.-M. Meng, H. Xie, Y.-Q. Fan and Y. Guo

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 equational 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 $[Mn(acac)_2(OH_2)_2]ClO_4].2H_2O$. (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).

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 $C_{12}H_{18}MnNO_5S$: C 41.99, H 5.29, N 4.08; found: C 42.04, H 5.26, N, 4.11.

Refinement

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

Figures

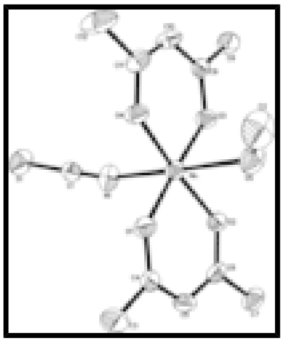

Fig. 1. A view of the title complex with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted.

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

Crystal data

$[Mn(C_5H_7O_2)_2(NCS)(CH_4O)]$	F_{000} = 712
M_r = 343.27	D_x = 1.412 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P2yn	Cell parameters from 1347 reflections
a = 7.4795 (13) Å	θ = 2.8?–16.2º
b = 12.420 (2) Å	μ = 0.96 mm^{-1}
c = 17.586 (3) Å	T = 293 (2) K
β = 98.673 (4)º	Block, brown
V = 1614.9 (5) Å^3	0.21 × 0.19 × 0.15 mm
Z = 4	

Data collection

Bruker APEXII CCD area-detector diffractometer	2830 independent reflections
Radiation source: fine-focus sealed tube	1276 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.112
T = 293(2) K	θ_{max} = 25.0º
φ and ω scans	θ_{min} = 2.0º
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	$h = -8 \rightarrow 8$
T_{min} = 0.824, T_{max} = 0.869	$k = -14 \rightarrow 14$
7925 measured reflections	$l = -16 \rightarrow 20$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement

$R[F^2 > 2\sigma(F^2)] = 0.058$	$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.148$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.91$	$\Delta\rho_{max} = 0.33$ e Å^{-3}
2830 reflections	$\Delta\rho_{min} = -0.33$ e Å^{-3}
189 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{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 (Å^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 (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5A···S1^{i}	0.78 (7)	2.51 (6)	3.281 (4)	168 (7)

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

Fig. 1