



Crystal structure and thermal properties of bis[μ -2-(methoxycarbonylhydrazinylidene)acetato- $\kappa^3N^1,O:O$]bis[diaqua(thiocyanato- κN)-manganese(II)] tetrahydrate

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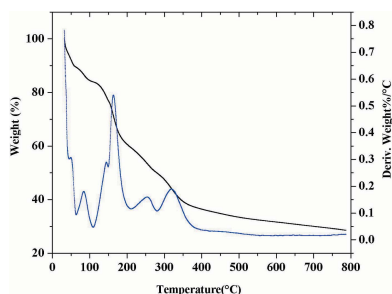
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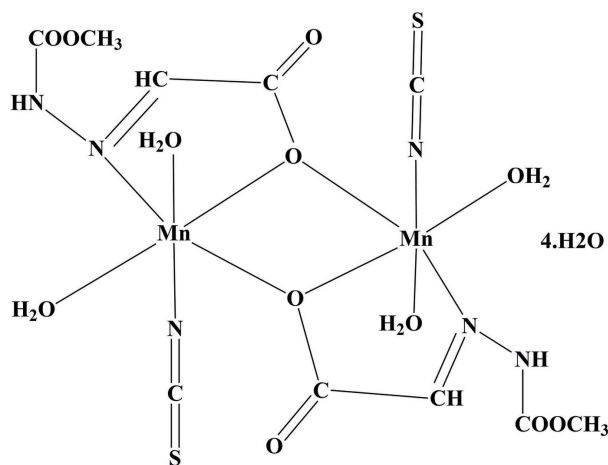
The title compound, $[\text{Mn}_2(\text{C}_4\text{H}_5\text{N}_2\text{O}_4)_2(\text{NCS})_2(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$ (I), exists as a centrosymmetric dimer. Each dimeric unit consists of tridentate (O,O,N)-chelating Schiff bases with symmetry-maintained μ - O -bridged carboxylate anions, terminally bound thiocyanate anions, and ligated and solvated water molecules. The complex exhibits a distorted octahedron geometry and the centrosymmetric μ - O -bridged carboxylate anions connect the two manganese atoms to form an M_2O_2 ring. In the crystal, the molecules are interlinked *via* strong $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonding contacts and weak $\text{O}-\text{H}\cdots\text{S}$ intermolecular interactions, forming a three-dimensional molecular network.

1. Chemical context

Hydrazine, dinitrogen tetrahydride (N_2H_4), is the simplest diamine and parent of innumerable organic derivatives. Among them, carbazates (esters of hydrazinecarboxylic acid, $\text{NH}_2\text{-NH-COO-R}$, where $R = \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}_2\text{C}_6\text{H}_5$ etc) are interesting as ligands in view of their variety of potential donor atoms such as oxygen and nitrogen. Interestingly, these neutral molecules can be expected to exhibit only one common coordination mode, *i.e.* N,O -chelating bidentate. This has been clearly observed in many metal complexes with a variety of anions such as formate (Srinivasan *et al.*, 2011), benzoate (Kathiresan *et al.*, 2012), thiocyanate (Srinivasan *et al.*, 2014*a,b*), nitrate (Zhang *et al.*, 2005; Srinivasan *et al.*, 2007,2008) and perchlorate (Chen *et al.*, 2016, Sitong *et al.*, 2016). Apart from their coordination ability, alkyl carbazates can also undergo condensation reactions; the hydrazinic part of the terminal amine group can react with the carbonyl group of aldehydes or ketones to form Schiff bases. In this regard, Schiff bases and their Co^{III} , Ni^{II} , Pd^{II} and Fe^{II} complexes based on (2-phenylphosphino)benzaldehyde with ethyl carbazate (Milenković *et al.*, 2013*a,b*, 2014) have been reported. Recently, we have also reported Schiff bases generated from analogous benzyl carbazate with alkyl and heteroaryl ketones, and their metal complexes (Nithya *et al.*, 2016, 2017*a,b*, 2018*a,b*). However, no work involving Schiff base complexes of alkyl carbazates with an aldehydic, or α -keto acid, has been reported so far, except from our own



recent report of a Schiff base generated from methyl carbazate and α -ketoglutaric acid, and its silver(I) complex (Parveen *et al.*, 2018). In a continuation of our investigations, the title complex (I) was prepared by a template method starting from manganese(II) nitrate with a Schiff base ligand. The product of condensation between methyl carbazate and glyoxylic acid, formed *in situ* in aqueous solution containing ammonium thiocyanate.



2. Structural commentary

2.1. General structural details

The manganese title compound crystallizes in the monoclinic space group $P2_1/n$ and exists as a centrosymmetric dimer (Fig. 1). The asymmetric unit consists of an Mn atom, a tridentate Schiff base ligand, an N-bounded thiocyanate moiety, and two ligated and two solvated water molecules. The manganese atom is surrounded in a distorted octahedral geometry by symmetry-related μ -O-bridged carboxylate anions, one azomethine nitrogen, an N-bounded NCS anion and two ligated water molecules with an MnN_2O_4 core. The

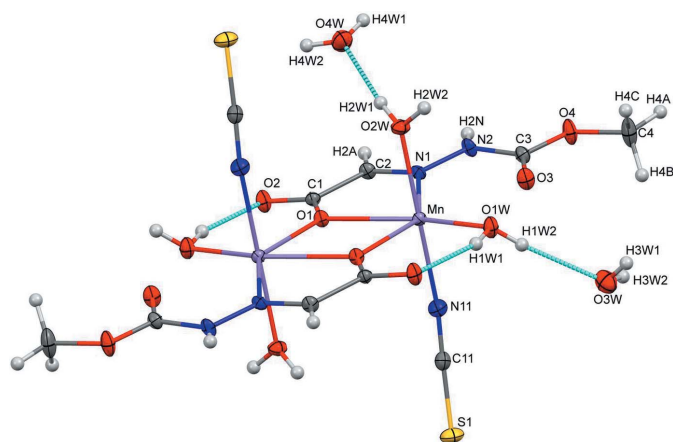


Figure 1

Molecular structure of the title complex (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. The molecule is located about an inversion centre and the unlabelled atoms are generated by the symmetry operation $(-x + 1, -y, -z + 1)$.

axial sites are occupied by one of the coordinated water molecules (O2W) and the N-bonded NCS anion, whereas the μ -O-bridged carboxylate anions, azomethine nitrogen atom and a coordinated water molecule (O1W) occupy the equatorial positions. The two manganese atoms are connected *via* centrosymmetrically related μ -O-bridged carboxylate anions, forming a rhomboidal Mn_2O_2 unit about an inversion centre.

2.2. Specific structural details

The separation of the Mn atoms is 3.645 (3) Å. The Mn–N(isothiocyanato) and Mn–N(azomethine) distances are 2.1289 (11) and 2.3388 (10) Å and the Mn–O distances involving the coordinated water molecules and μ -O-bridged carboxylate anions are 2.1448 (9), 2.1905 (9) and 2.2606 (8), 2.2985 (8) Å, respectively. The Mn–N–C–S torsion angle in the NCS moiety is 103.5 (4) and the bond angles for the coordinated atoms vary from 68.99 (3)–132.57 (4), indicating a distorted geometry.

3. Supramolecular features

The crystal structure of (I) contains both coordinated and solvated water molecules. Inter- and intra-molecular hydrogen-bonding interactions (Table 1) stabilize the supramolecular three-dimensional network. The $N2-H2N \cdots O2^v$ [2.7971 (13) Å] hydrogen bond between adjacent dimers forms chains extending along the *ac* diagonal. The weak $O4W-H4W1 \cdots S1^{iv}$ interaction [3.3159 (12) Å] and $O2W-H2W1 \cdots O4W$ hydrogen bond [2.7322 (14) Å] link the dimers, generating a two-dimensional network as shown in Fig. 2. The ligated and solvated water molecules O1W, O3W and O4W are involved in $O-H \cdots O$ hydrogen-bonding interactions [2.733 (14)–3.2158 (15) Å, Table 1] that stack the complex

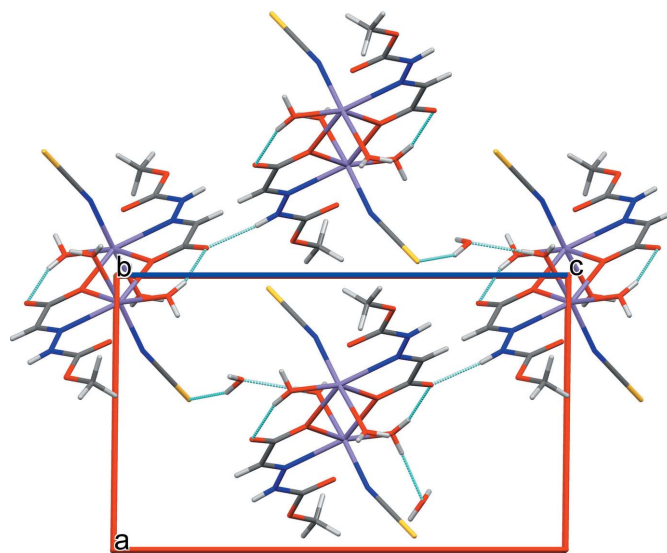


Figure 2

View of a two-dimensional array of (I) showing N–H \cdots O and O–H \cdots O hydrogen bonds and weak O–H \cdots S intermolecular interactions (green lines) in a projection along the *b* axis.

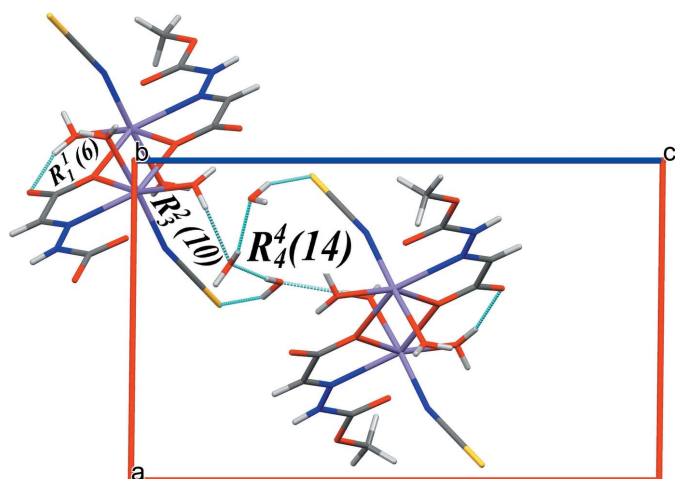


Figure 3
View of hydrogen-bonding interactions (green lines) along the *ac* plane forming various ring motifs to further stabilize the three-dimensional network.

molecules along the *b*-axis direction. These contacts combine to generate several ring motifs (Fig. 3) *viz.* $R_1^1(6)$, $R_3^2(10)$ and $R_4^4(14)$ that stabilize the three-dimensional supramolecular network (Fig. 4).

4. Thermal properties

The thermal decomposition behaviour of the title complex was studied by simultaneous TG–DTG analyses recorded in a nitrogen atmosphere in the temperature range 30–800°C, as shown in Fig. 5. The TG curve displays the combined mass loss of 20.5% (calculated 21.8%) in the temperature range 30–

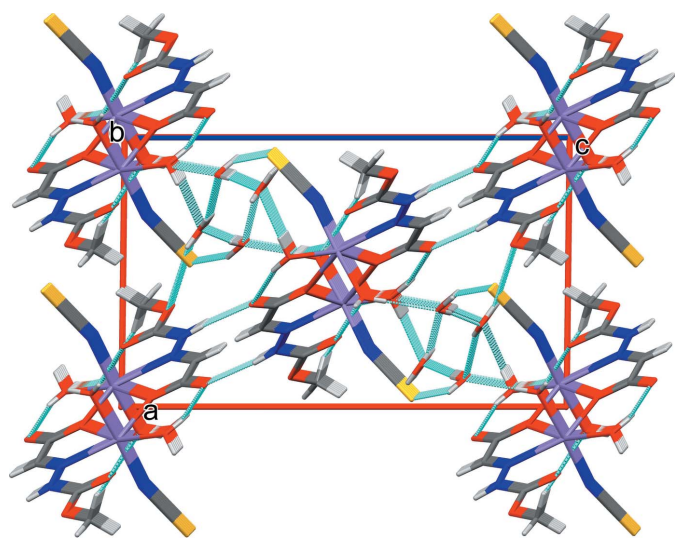


Figure 4
Overall packing view of the three-dimensional network for (I), viewed along the *b* axis, showing N–H...O and O–H...O hydrogen bonds and weak O–H...S intermolecular interactions (green lines) and the stacking of (I) along the *b* axis.

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

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O1W–H1W1...O2 ⁱ	0.83 (2)	1.92 (2)	2.7158 (13)	160 (2)
O1W–H1W2...O3W	0.80 (2)	2.07 (2)	2.8627 (15)	174 (2)
O2W–H2W1...O4W	0.79 (2)	1.94 (2)	2.7332 (14)	175 (2)
O2W–H2W2...O3 ⁱⁱ	0.82 (3)	2.11 (3)	2.8852 (13)	159 (2)
O2W–H2W2...O1W ⁱⁱ	0.82 (3)	2.54 (2)	3.0865 (13)	125 (2)
O3W–H3W1...O4W ⁱⁱ	0.79 (2)	2.09 (3)	2.8264 (17)	155 (2)
O3W–H3W2...O4 ⁱⁱⁱ	0.80 (3)	2.54 (3)	3.2158 (15)	144 (2)
O4W–H4W1...S1 ^{iv}	0.87 (3)	2.52 (3)	3.3159 (12)	153 (2)
O4W–H4W2...O3W ^{iv}	0.81 (2)	1.97 (2)	2.7754 (16)	173 (2)
N2–H2N...O2 ^v	0.83 (2)	1.97 (2)	2.7971 (13)	174 (2)

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

140°C corresponding to dehydration of both the solvated and coordinated water molecules. The anhydrous compound then shows continuous decomposition between 140 and 600°C to give manganese sulfide as the end product (mass loss observed 73.6%, calculated 72.50%). The DTG curve shows a doublet (40 and 80°C) for dehydration and a multiplet (150, 164, 255 and 321°C) for the decomposition of the anhydrous compound in accordance with TG mass loss.

5. Database survey

There are a few structures of metal complexes in the crystallographic literature with simple hydrazones based on glyoxylic acid and salicyloyl hydrazine (Liu *et al.*, 2010) and thiosemicarbazide (Dodoff *et al.*, 2006; Huseynova *et al.*, 2018). In the former salicyloyl hydrazone complex of cadmium, the Schiff base acts as a tetradentate (*O,N,O,O*) ligand with one of the carboxylate oxygen atoms bridging the cadmium centers, leading to a dimer, whereas in the thiosemicarbazone complexes of Zn, Pd, Pt, Co, and Ni (Milenković *et al.*, 2013*a,b*, 2014), the ligand adopts a tridentate (*O,N,O*) coordination mode. Recently, we have reported a silver(I) complex of

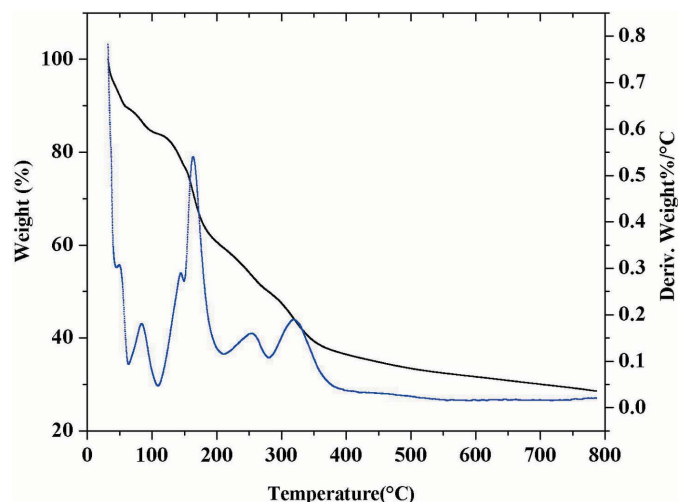


Figure 5
Simultaneous TG/DTG (N₂ atmosphere) analysis of the title complex (I).

Table 2
Experimental details.

Crystal data	
Chemical formula	$[\text{Mn}_2(\text{C}_4\text{H}_5\text{N}_2\text{O}_4)_2(\text{NCS})_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$
M_r	660.37
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	120
a, b, c (Å)	9.7060 (3), 8.3654 (3), 16.0082 (6)
β (°)	90.653 (2)
V (Å ³)	1299.69 (8)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	1.21
Crystal size (mm)	0.46 × 0.24 × 0.17
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 1996)
$T_{\text{min}}, T_{\text{max}}$	0.658, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12223, 3915, 3408
R_{int}	0.024
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.715
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.025, 0.060, 1.05
No. of reflections	3915
No. of parameters	200
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.49, -0.34

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SIR92* (Altomare *et al.*, 1993), *SHELXL2018/3* (Sheldrick, 2015) and *shelXle* (Hübschle *et al.*, 2011).

2-(methoxycarbonylhydrazono)pentanedioic acid in which the neutral as well as monoanionic Schiff base behaves as a tridentate (*O,N,O*) group, leading to an octahedral coordination of the silver atom (Parveen *et al.*, 2018).

6. Synthesis and crystallization

Elemental analyses for carbon, hydrogen and nitrogen were recorded using a Vario-ELIII elemental analyzer. The IR spectrum was recorded using a JASCO-4100 spectrophotometer and KBr pellets in the range of 4000–400.00 cm⁻¹. Simultaneous TG/DTG (TG/DTG) analyses were carried out using a TA instrument, SDT Q600 thermal analyzer, in a flowing nitrogen atmosphere with a heating rate of 10°C min⁻¹.

Stoichiometric quantities of glyoxylic acid (0.184 g, 2 mmol), ethylcarbazate (0.208 g, 2 mmol) and ammonium thiocyanate (0.152 g, 2 mmol) were dissolved in 30 mL of double-distilled water. To this homogeneous solution, Mn(NO₃)₂·6H₂O (0.287 g, 1 mmol) dissolved in 10.00 mL of double-distilled water was added dropwise, the pH of the resulting solution was noted as 3.45. The above clear solution was kept over a water-bath until the solution was reduced to ca 15 mL and allowed to stand at room temperature for slow crystallization. After two days, colourless rod-shaped crystals were obtained and filtered off, washed with ice-cold water and air dried. The product is soluble in water, methanol and

ethanol and insoluble in diethyl ether. In the absence of ammonium thiocyanate, the reaction did not yield any desired product. Yield: 64%. Analysis calculated for C₁₀H₂₆Mn₂N₆O₁₆S₂ (I): C, 29.25, H, 3.44, N, 13.57; found: C, 29.20; H, 3.49; N, 13.55. Metal (%): calculated 14.27 (found: 14.06), FT-IR (KBr, cm⁻¹): 3520 (*b*) [$\nu(\text{O}-\text{H})$], 3206 (*b*) [$\nu(\text{N}-\text{H})$], 2096 (*s*) [$\nu(\text{C}\equiv\text{N})$], 1705 (*s*) [$\nu(\text{C}=\text{O})$], 1627 (*m*) [$\nu_{\text{asym}}(\text{C}=\text{O})$], 1555 (*s*) [$\nu(\text{C}=\text{N})$], 1397 (*s*) [$\nu_{\text{sym}}(\text{C}=\text{O})$], 1067 (*s*) [$\nu(\text{N}-\text{N})$].

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms attached to carbon atoms were positioned geometrically and constrained to ride on their parent atoms, with carbon–hydrogen bond lengths of 0.95 Å for alkene C–H and 0.98 Å for CH₃ groups, respectively. Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. $U_{\text{iso}}(\text{H})$ values were set to a multiple of $U_{\text{eq}}(\text{C})$ with 1.5 for CH₃ and 1.2 for C–H groups, respectively. Positions and U_{iso} values of water and amine H atoms were freely refined.

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supporting information

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Crystal structure and thermal properties of bis[μ -2-(methoxycarbonylhydrazinylidene)acetato- $\kappa^3 N^1, O:O$]bis[diaqua(thiocyanato- κN)manganese(II)] tetrahydrate

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Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINTE* (Bruker, 2014); data reduction: *SAINTE* (Bruker, 2014); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015) and *shelXle* (Hübschle *et al.*, 2011).

Bis[μ -2-(methoxycarbonylhydrazinylidene)acetato- $\kappa^3 N^1, O:O$]bis[diaqua(thiocyanato- κN)manganese(II)] tetrahydrate

Crystal data

[Mn₂(C₄H₅N₂O₄)₂(NCS)₂(H₂O)₄].4H₂O

$M_r = 660.37$

Monoclinic, *P2₁/n*

$a = 9.7060$ (3) Å

$b = 8.3654$ (3) Å

$c = 16.0082$ (6) Å

$\beta = 90.653$ (2)°

$V = 1299.69$ (8) Å³

$Z = 2$

$F(000) = 676$

$D_x = 1.687$ Mg m⁻³

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

Cell parameters from 6980 reflections

$\theta = 2.5$ – 30.6 °

$\mu = 1.21$ mm⁻¹

$T = 120$ K

Rod, colourless

$0.46 \times 0.24 \times 0.17$ mm

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine focus sealed tube

Graphite monochromator

ω and ϕ scans

Absorption correction: multi-scan

(SADABS; Sheldrick, 1996)

$T_{\min} = 0.658$, $T_{\max} = 0.746$

12223 measured reflections

3915 independent reflections

3408 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 30.6$ °, $\theta_{\min} = 2.4$ °

$h = -13 \rightarrow 12$

$k = -11 \rightarrow 11$

$l = -22 \rightarrow 22$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.025$

$wR(F^2) = 0.060$

$S = 1.05$

3915 reflections

200 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0256P)^2 + 0.5439P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.003$

$$\Delta\rho_{\max} = 0.49 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.34 \text{ e } \text{\AA}^{-3}$$

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.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Mn1	0.59833 (2)	0.18522 (2)	0.50685 (2)	0.00920 (5)
S1	0.95128 (4)	-0.10626 (4)	0.66382 (2)	0.02029 (8)
O1	0.55108 (9)	-0.03030 (10)	0.42219 (5)	0.01108 (16)
O2	0.60023 (10)	-0.15606 (10)	0.30205 (5)	0.01546 (18)
O3	0.74296 (10)	0.44631 (11)	0.48516 (5)	0.01696 (18)
O4	0.87386 (10)	0.57439 (11)	0.38944 (6)	0.0191 (2)
O1W	0.57632 (11)	0.34713 (11)	0.61341 (6)	0.01577 (18)
H1W1	0.528 (2)	0.303 (3)	0.6488 (14)	0.046 (6)*
H1W2	0.646 (2)	0.379 (3)	0.6349 (14)	0.041 (6)*
O2W	0.42696 (10)	0.30284 (11)	0.44755 (6)	0.01524 (18)
H2W1	0.414 (2)	0.292 (2)	0.3989 (13)	0.028 (5)*
H2W2	0.396 (2)	0.389 (3)	0.4635 (15)	0.055 (7)*
O3W	0.82278 (12)	0.48163 (13)	0.68375 (7)	0.0247 (2)
H3W1	0.787 (3)	0.562 (3)	0.6975 (15)	0.053 (7)*
H3W2	0.887 (3)	0.509 (3)	0.6565 (16)	0.062 (8)*
O4W	0.38041 (13)	0.28790 (14)	0.27902 (7)	0.0265 (2)
H4W1	0.426 (3)	0.353 (3)	0.2471 (15)	0.057 (7)*
H4W2	0.370 (2)	0.206 (3)	0.2527 (14)	0.044 (6)*
N1	0.70220 (10)	0.21438 (11)	0.37662 (6)	0.01068 (19)
N2	0.77597 (11)	0.34553 (12)	0.35488 (6)	0.0123 (2)
H2N	0.8177 (18)	0.349 (2)	0.3097 (11)	0.018 (4)*
N11	0.77393 (12)	0.06901 (13)	0.55969 (7)	0.0184 (2)
C11	0.84668 (13)	-0.00547 (15)	0.60238 (8)	0.0140 (2)
C1	0.60689 (12)	-0.03982 (14)	0.35114 (7)	0.0107 (2)
C2	0.68949 (12)	0.10135 (14)	0.32384 (7)	0.0117 (2)
H2A	0.730139	0.106396	0.270198	0.014*
C3	0.79375 (13)	0.45612 (14)	0.41613 (7)	0.0125 (2)
C4	0.89246 (17)	0.70729 (17)	0.44739 (9)	0.0256 (3)
H4A	0.947018	0.791232	0.420758	0.038*
H4B	0.940626	0.669641	0.497796	0.038*
H4C	0.802229	0.750334	0.462554	0.038*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.01079 (9)	0.00955 (9)	0.00729 (8)	0.00015 (6)	0.00089 (6)	-0.00039 (6)

S1	0.01857 (16)	0.02354 (17)	0.01866 (15)	0.00707 (12)	-0.00337 (12)	0.00329 (13)
O1	0.0138 (4)	0.0112 (4)	0.0083 (4)	-0.0019 (3)	0.0033 (3)	-0.0009 (3)
O2	0.0215 (5)	0.0138 (4)	0.0113 (4)	-0.0043 (3)	0.0066 (3)	-0.0045 (3)
O3	0.0233 (5)	0.0163 (4)	0.0114 (4)	-0.0045 (4)	0.0061 (3)	-0.0022 (3)
O4	0.0254 (5)	0.0149 (4)	0.0170 (4)	-0.0098 (4)	0.0085 (4)	-0.0039 (3)
O1W	0.0211 (5)	0.0149 (4)	0.0114 (4)	-0.0064 (4)	0.0040 (4)	-0.0029 (3)
O2W	0.0185 (5)	0.0151 (4)	0.0121 (4)	0.0051 (3)	-0.0019 (3)	-0.0013 (3)
O3W	0.0230 (6)	0.0228 (5)	0.0284 (5)	-0.0034 (4)	0.0049 (4)	0.0034 (4)
O4W	0.0377 (6)	0.0246 (5)	0.0171 (5)	-0.0057 (5)	-0.0050 (4)	0.0004 (4)
N1	0.0108 (5)	0.0092 (4)	0.0121 (4)	-0.0004 (3)	0.0019 (3)	0.0019 (4)
N2	0.0165 (5)	0.0102 (4)	0.0102 (4)	-0.0032 (4)	0.0058 (4)	0.0003 (4)
N11	0.0173 (6)	0.0175 (5)	0.0202 (5)	0.0004 (4)	-0.0033 (4)	0.0005 (4)
C11	0.0130 (6)	0.0140 (5)	0.0151 (5)	-0.0015 (4)	0.0009 (4)	-0.0018 (4)
C1	0.0115 (5)	0.0107 (5)	0.0098 (5)	-0.0003 (4)	0.0005 (4)	0.0002 (4)
C2	0.0139 (6)	0.0123 (5)	0.0090 (5)	-0.0004 (4)	0.0033 (4)	0.0002 (4)
C3	0.0125 (6)	0.0113 (5)	0.0136 (5)	-0.0009 (4)	0.0027 (4)	0.0004 (4)
C4	0.0331 (8)	0.0186 (6)	0.0254 (7)	-0.0131 (6)	0.0074 (6)	-0.0091 (5)

Geometric parameters (Å, °)

Mn1—N11	2.1289 (11)	O2W—H2W2	0.82 (3)
Mn1—O2W	2.1448 (9)	O3W—H3W1	0.79 (2)
Mn1—O1W	2.1905 (9)	O3W—H3W2	0.80 (3)
Mn1—O1 ⁱ	2.2606 (8)	O4W—H4W1	0.87 (3)
Mn1—O1	2.2985 (8)	O4W—H4W2	0.81 (2)
Mn1—N1	2.3388 (10)	N1—C2	1.2731 (15)
Mn1—O3	2.6216 (9)	N1—N2	1.3576 (14)
S1—C11	1.6390 (13)	N2—C3	1.3577 (15)
O1—C1	1.2679 (13)	N2—H2N	0.833 (17)
O2—C1	1.2515 (14)	N11—C11	1.1588 (17)
O3—C3	1.2177 (14)	C1—C2	1.4955 (16)
O4—C3	1.3318 (14)	C2—H2A	0.9500
O4—C4	1.4578 (16)	C4—H4A	0.9800
O1W—H1W1	0.83 (2)	C4—H4B	0.9800
O1W—H1W2	0.80 (2)	C4—H4C	0.9800
O2W—H2W1	0.79 (2)		
N11—Mn1—O2W	177.02 (4)	Mn1—O2W—H2W1	119.7 (14)
N11—Mn1—O1W	93.31 (4)	Mn1—O2W—H2W2	123.1 (17)
O2W—Mn1—O1W	88.79 (4)	H2W1—O2W—H2W2	111 (2)
N11—Mn1—O1 ⁱ	93.09 (4)	H3W1—O3W—H3W2	105 (2)
O2W—Mn1—O1 ⁱ	89.24 (3)	H4W1—O4W—H4W2	106 (2)
O1W—Mn1—O1 ⁱ	83.93 (3)	C2—N1—N2	118.52 (10)
N11—Mn1—O1	91.69 (4)	C2—N1—Mn1	118.34 (8)
O2W—Mn1—O1	87.15 (3)	N2—N1—Mn1	123.15 (7)
O1W—Mn1—O1	157.45 (3)	N1—N2—C3	115.37 (10)
O1 ⁱ —Mn1—O1	73.84 (3)	N1—N2—H2N	120.8 (12)
N11—Mn1—N1	92.90 (4)	C3—N2—H2N	123.0 (12)

O2W—Mn1—N1	84.12 (4)	C11—N11—Mn1	163.64 (10)
O1W—Mn1—N1	132.57 (4)	N11—C11—S1	178.43 (12)
O1 ⁱ —Mn1—N1	142.48 (3)	O2—C1—O1	126.34 (11)
O1—Mn1—N1	68.99 (3)	O2—C1—C2	117.00 (10)
N11—Mn1—O3	90.32 (4)	O1—C1—C2	116.65 (10)
O2W—Mn1—O3	88.45 (3)	N1—C2—C1	116.15 (10)
O1W—Mn1—O3	69.22 (3)	N1—C2—H2A	121.9
O1 ⁱ —Mn1—O3	153.09 (3)	C1—C2—H2A	121.9
O1—Mn1—O3	132.76 (3)	O3—C3—O4	125.80 (11)
N1—Mn1—O3	63.78 (3)	O3—C3—N2	124.05 (11)
C1—O1—Mn1 ⁱ	134.25 (7)	O4—C3—N2	110.14 (10)
C1—O1—Mn1	119.59 (7)	O4—C4—H4A	109.5
Mn1 ⁱ —O1—Mn1	106.16 (3)	O4—C4—H4B	109.5
C3—O3—Mn1	113.53 (8)	H4A—C4—H4B	109.5
C3—O4—C4	115.53 (10)	O4—C4—H4C	109.5
Mn1—O1W—H1W1	108.5 (15)	H4A—C4—H4C	109.5
Mn1—O1W—H1W2	116.8 (16)	H4B—C4—H4C	109.5
H1W1—O1W—H1W2	110 (2)		
C2—N1—N2—C3	-175.42 (11)	O2—C1—C2—N1	-175.83 (11)
Mn1—N1—N2—C3	4.17 (14)	O1—C1—C2—N1	3.73 (16)
Mn1 ⁱ —O1—C1—O2	-7.27 (19)	Mn1—O3—C3—O4	-178.58 (10)
Mn1—O1—C1—O2	173.28 (10)	Mn1—O3—C3—N2	1.36 (16)
Mn1 ⁱ —O1—C1—C2	173.21 (8)	C4—O4—C3—O3	-4.53 (19)
Mn1—O1—C1—C2	-6.24 (13)	C4—O4—C3—N2	175.52 (12)
N2—N1—C2—C1	-179.86 (10)	N1—N2—C3—O3	-3.54 (18)
Mn1—N1—C2—C1	0.53 (14)	N1—N2—C3—O4	176.40 (10)

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1W—H1W1...O2 ⁱ	0.83 (2)	1.92 (2)	2.7158 (13)	160 (2)
O1W—H1W2...O3W	0.80 (2)	2.07 (2)	2.8627 (15)	174 (2)
O2W—H2W1...O4W	0.79 (2)	1.94 (2)	2.7332 (14)	174.6 (19)
O2W—H2W2...O3 ⁱⁱ	0.82 (3)	2.11 (3)	2.8852 (13)	159 (2)
O2W—H2W2...O1W ⁱⁱ	0.82 (3)	2.54 (2)	3.0865 (13)	125 (2)
O3W—H3W1...O4W ⁱⁱ	0.79 (2)	2.09 (3)	2.8264 (17)	155 (2)
O3W—H3W2...O4 ⁱⁱⁱ	0.80 (3)	2.54 (3)	3.2158 (15)	144 (2)
O4W—H4W1...S1 ^{iv}	0.87 (3)	2.52 (3)	3.3159 (12)	153 (2)
O4W—H4W2...O3W ^{iv}	0.81 (2)	1.97 (2)	2.7754 (16)	173 (2)
N2—H2N...O2 ^v	0.833 (17)	1.967 (17)	2.7971 (13)	173.9 (17)

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+2, -y+1, -z+1$; (iv) $x-1/2, -y+1/2, z-1/2$; (v) $-x+3/2, y+1/2, -z+1/2$.