



# Crystal structure of bis(4-acetylpyridine- $\kappa N$ )bis(ethanol- $\kappa O$ )bis(thiocyanato- $\kappa N$ )-manganese(II)

Julia Werner,\* Inke Jess and Christian Näther

Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel, Max-Eyth-Strasse 2, 24118 Kiel, Germany. \*Correspondence e-mail: jwerner@ac.uni-kiel.de

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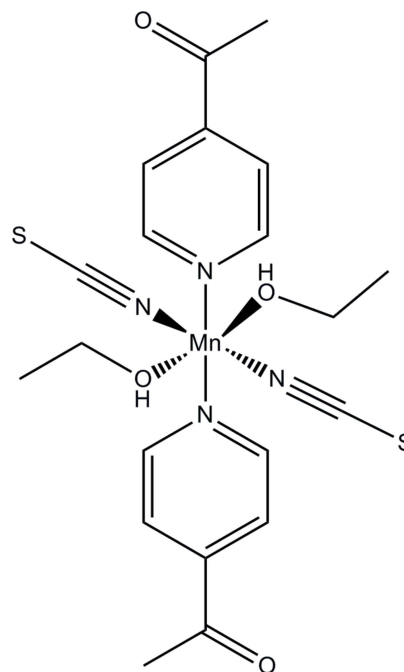
In the crystal structure of the title compound,  $[\text{Mn}(\text{NCS})_2(\text{C}_7\text{H}_7\text{NO})_2(\text{C}_2\text{H}_5\text{OH})_2]$ , the  $\text{Mn}^{\text{II}}$  atom is coordinated by two  $N$ -bonded thiocyanate anions, two 4-acetylpyridine ligands, and two ethanol molecules within a slightly distorted octahedron. The asymmetric unit consists of one manganese cation, located on a centre of inversion, one thiocyanate anion, one 4-acetylpyridine ligand and one ethanol molecule in general positions. The discrete complexes are connected by intermolecular  $\text{O} \cdots \text{H} \cdots \text{O}$  hydrogen bonds between the alcohol OH group and the carbonyl O atom into chains parallel to  $[011]$ .

**Keywords:** crystal structure; manganese(II); octahedral coordination; hydrogen bonding.

**CCDC reference:** 1052202

## 1. Related literature

For a similar structure with thiocyanato ligands in terminal coordination to a manganese(II) atom, see: Li *et al.* (2007).



## 2. Experimental

### 2.1. Crystal data

$[\text{Mn}(\text{NCS})_2(\text{C}_7\text{H}_7\text{NO})_2(\text{C}_2\text{H}_6\text{O})_2]$   
 $M_r = 505.51$   
 Triclinic,  $P\bar{1}$   
 $a = 6.9547$  (7) Å  
 $b = 9.7733$  (9) Å  
 $c = 10.1859$  (9) Å  
 $\alpha = 117.449$  (10)°  
 $\beta = 94.978$  (11)°

$\gamma = 93.379$  (11)°  
 $V = 608.23$  (11) Å<sup>3</sup>  
 $Z = 1$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.75$  mm<sup>-1</sup>  
 $T = 200$  K  
 $0.04 \times 0.03 \times 0.02$  mm

### 2.2. Data collection

Stoe IPDS-1 diffractometer  
 Absorption correction: numerical  
 (*X-SHAPE* and *X-RED32*; Stoe & Cie, 2008)  
 $T_{\min} = 0.966$ ,  $T_{\max} = 0.977$

6535 measured reflections  
 2583 independent reflections  
 2163 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.039$

### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.088$   
 $S = 1.04$   
 2583 reflections

144 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.26$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.35$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$                               | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|----------------------------------------------|-------|--------------|--------------|----------------|
| $\text{O21}-\text{H1O1} \cdots \text{O11}^i$ | 0.84  | 1.95         | 2.7714 (17)  | 164            |

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

Data collection: *X-Area* (Stoe & Cie, 2008); cell refinement: *X-Area*; data reduction: *X-Area*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure:

*SHELXL2013* (Sheldrick, 2015); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: WM5131).

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### References

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## supporting information

*Acta Cryst.* (2015). E71, m81–m82 [doi:10.1107/S2056989015004533]

## Crystal structure of bis(4-acetylpyridine- $\kappa N$ )bis(ethanol- $\kappa O$ )bis(thiocyanato- $\kappa N$ )manganese(II)

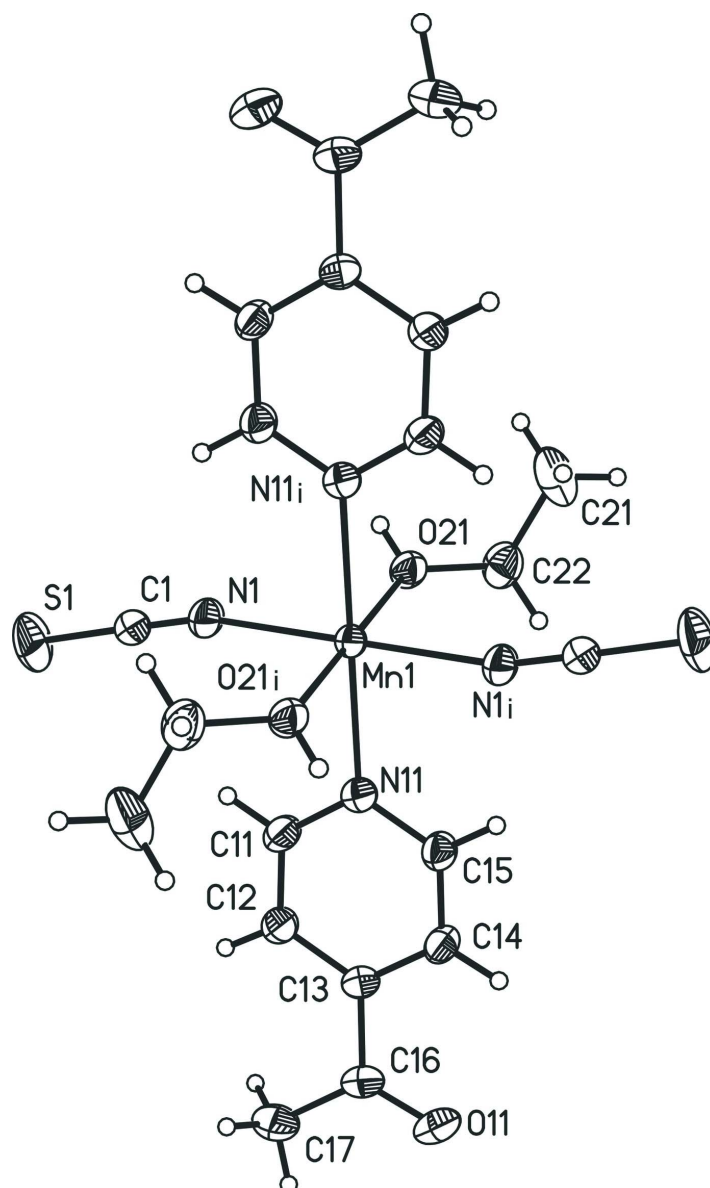
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### S1. Synthesis and crystallization

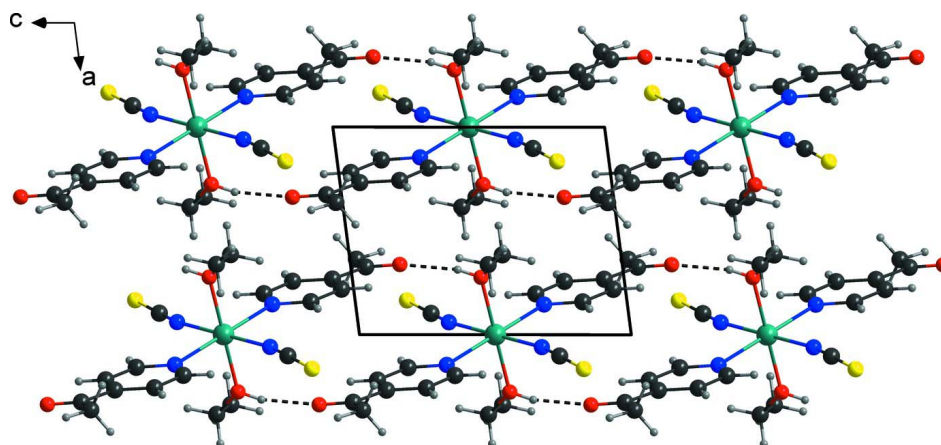
MnSO<sub>4</sub>·H<sub>2</sub>O was purchased from Merck; 4-acetylpyridine and Ba(NCS)<sub>2</sub>·3H<sub>2</sub>O were purchased from Alfa Aesar. Mn(NCS)<sub>2</sub> was synthesized by stirring 17.97 g (58.44 mmol) Ba(NCS)<sub>2</sub>·3H<sub>2</sub>O and 9.88 g (58.44 mmol) MnSO<sub>4</sub>·H<sub>2</sub>O in 400 ml water at room temperature for three hours. The white residue of BaSO<sub>4</sub> was filtered off and the solvent evaporated using a rotary evaporator. The homogeneity of the product was investigated by X-ray powder diffraction and elemental analysis. The title compound was prepared by the reaction of 42.8 mg (0.25 mmol) Mn(NCS)<sub>2</sub> and 55.1  $\mu$ l (0.50 mmol) 4-acetylpyridine in 1.5 ml ethanol at room temperature. After several days, suitable crystals of the title compound were obtained.

### S2. Refinement

The C-bound H atoms were positioned with idealized geometry (methyl H atoms allowed to rotate but not to tip) and were refined with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  (1.5 for methyl H atoms) using a riding model with C—H = 0.95 Å for aromatic, C—H = 0.99 Å for methylene and C—H = 0.98 Å for methyl H atoms. The O-bound H atom was located in a difference map. Its bond length was set to a value of 0.84 Å and it was refined with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$  using a riding model.

**Figure 1**

The coordination environment of the Mn<sup>II</sup> atom in the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i)  $-x + 2, -y + 1, -z + 1$ .]

**Figure 2**

Crystal structure of the title compound in a view along [010]. Hydrogen bonds are indicated by dashed lines.

**Bis(ethanol- $\kappa$ O)bis[1-(pyridin-4-yl)ethan-1-one- $\kappa$ N]bis(thiocyanato- $\kappa$ N)manganese(II)**

*Crystal data*

[Mn(NCS)<sub>2</sub>(C<sub>7</sub>H<sub>7</sub>NO)<sub>2</sub>(C<sub>2</sub>H<sub>6</sub>O)<sub>2</sub>]

$M_r = 505.51$

Triclinic,  $P\bar{1}$

$a = 6.9547$  (7) Å

$b = 9.7733$  (9) Å

$c = 10.1859$  (9) Å

$\alpha = 117.449$  (10)°

$\beta = 94.978$  (11)°

$\gamma = 93.379$  (11)°

$V = 608.23$  (11) Å<sup>3</sup>

$Z = 1$

$F(000) = 263$

$D_x = 1.380$  Mg m<sup>-3</sup>

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

Cell parameters from 6535 reflections

$\theta = 2.4$ – $27.0^\circ$

$\mu = 0.75$  mm<sup>-1</sup>

$T = 200$  K

Block, colorless

$0.04 \times 0.03 \times 0.02$  mm

*Data collection*

Stoe IPDS-1

diffractometer

phi scans

Absorption correction: numerical

(*X-SHAPE* and *X-RED32*; Stoe & Cie, 2008)

$T_{\min} = 0.966$ ,  $T_{\max} = 0.977$

6535 measured reflections

2583 independent reflections

2163 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

$\theta_{\max} = 27.0^\circ$ ,  $\theta_{\min} = 2.4^\circ$

$h = -8 \rightarrow 8$

$k = -12 \rightarrow 12$

$l = -13 \rightarrow 13$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.088$

$S = 1.04$

2583 reflections

144 parameters

0 restraints

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0565P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.26$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.35$  e Å<sup>-3</sup>

Extinction correction: *SHELXL2013* (Sheldrick, 2015),  $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.069 (8)

*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 ( $\text{\AA}^2$ )*

|      | <i>x</i>     | <i>y</i>      | <i>z</i>      | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|---------------|---------------|----------------------------------|
| Mn1  | 1.0000       | 0.5000        | 0.5000        | 0.02081 (14)                     |
| N1   | 0.9402 (2)   | 0.42929 (18)  | 0.66517 (15)  | 0.0300 (3)                       |
| C1   | 0.8976 (2)   | 0.35987 (19)  | 0.72660 (17)  | 0.0245 (3)                       |
| S1   | 0.83508 (10) | 0.25963 (7)   | 0.80913 (7)   | 0.05345 (19)                     |
| N11  | 0.8542 (2)   | 0.25989 (15)  | 0.30663 (15)  | 0.0250 (3)                       |
| C11  | 0.8030 (3)   | 0.1414 (2)    | 0.33223 (19)  | 0.0339 (4)                       |
| H11  | 0.8081       | 0.1609        | 0.4329        | 0.041*                           |
| C12  | 0.7431 (3)   | −0.0080 (2)   | 0.22080 (19)  | 0.0338 (4)                       |
| H12  | 0.7099       | −0.0886       | 0.2451        | 0.041*                           |
| C13  | 0.7325 (2)   | −0.03842 (18) | 0.07316 (17)  | 0.0241 (3)                       |
| C14  | 0.7813 (3)   | 0.0837 (2)    | 0.04487 (18)  | 0.0276 (4)                       |
| H14  | 0.7738       | 0.0676        | −0.0549       | 0.033*                           |
| C15  | 0.8413 (3)   | 0.2296 (2)    | 0.16300 (18)  | 0.0278 (4)                       |
| H15  | 0.8749       | 0.3123        | 0.1417        | 0.033*                           |
| C16  | 0.6741 (3)   | −0.19848 (19) | −0.05499 (18) | 0.0285 (4)                       |
| C17  | 0.6365 (3)   | −0.3314 (2)   | −0.0243 (2)   | 0.0417 (5)                       |
| H17A | 0.6077       | −0.4275       | −0.1188       | 0.063*                           |
| H17B | 0.5254       | −0.3158       | 0.0322        | 0.063*                           |
| H17C | 0.7515       | −0.3384       | 0.0341        | 0.063*                           |
| O11  | 0.6621 (2)   | −0.21465 (16) | −0.18155 (14) | 0.0409 (3)                       |
| C21  | 0.6624 (4)   | 0.8271 (3)    | 0.4935 (3)    | 0.0549 (6)                       |
| H21A | 0.5856       | 0.8597        | 0.4296        | 0.082*                           |
| H21B | 0.6313       | 0.8831        | 0.5958        | 0.082*                           |
| H21C | 0.8010       | 0.8504        | 0.4921        | 0.082*                           |
| C22  | 0.6154 (3)   | 0.6558 (2)    | 0.4366 (2)    | 0.0367 (4)                       |
| H22A | 0.4748       | 0.6326        | 0.4363        | 0.044*                           |
| H22B | 0.6445       | 0.5999        | 0.3325        | 0.044*                           |
| O21  | 0.72349 (18) | 0.60072 (14)  | 0.52571 (12)  | 0.0291 (3)                       |
| H1O1 | 0.6854       | 0.6446        | 0.6101        | 0.044*                           |

*Atomic displacement parameters ( $\text{\AA}^2$ )*

|     | $U^{11}$    | $U^{22}$     | $U^{33}$     | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|-----|-------------|--------------|--------------|--------------|--------------|--------------|
| Mn1 | 0.0266 (2)  | 0.01896 (19) | 0.01844 (18) | 0.00180 (12) | 0.00503 (13) | 0.00984 (14) |
| N1  | 0.0409 (9)  | 0.0290 (7)   | 0.0236 (7)   | 0.0005 (6)   | 0.0079 (6)   | 0.0150 (6)   |
| C1  | 0.0280 (8)  | 0.0232 (7)   | 0.0217 (7)   | 0.0021 (6)   | 0.0039 (6)   | 0.0099 (6)   |
| S1  | 0.0678 (4)  | 0.0535 (4)   | 0.0652 (4)   | 0.0037 (3)   | 0.0157 (3)   | 0.0489 (3)   |
| N11 | 0.0295 (7)  | 0.0219 (7)   | 0.0220 (6)   | 0.0014 (5)   | 0.0027 (5)   | 0.0091 (6)   |
| C11 | 0.0525 (12) | 0.0266 (8)   | 0.0206 (7)   | −0.0014 (8)  | 0.0051 (7)   | 0.0099 (7)   |

|     |             |             |             |             |             |             |
|-----|-------------|-------------|-------------|-------------|-------------|-------------|
| C12 | 0.0539 (12) | 0.0225 (8)  | 0.0245 (8)  | −0.0016 (8) | 0.0056 (8)  | 0.0111 (7)  |
| C13 | 0.0237 (8)  | 0.0241 (7)  | 0.0219 (7)  | 0.0041 (6)  | 0.0051 (6)  | 0.0080 (6)  |
| C14 | 0.0323 (9)  | 0.0305 (8)  | 0.0194 (7)  | 0.0012 (7)  | 0.0039 (6)  | 0.0114 (7)  |
| C15 | 0.0338 (9)  | 0.0267 (8)  | 0.0240 (7)  | −0.0015 (7) | 0.0026 (7)  | 0.0136 (7)  |
| C16 | 0.0273 (8)  | 0.0258 (8)  | 0.0254 (8)  | 0.0060 (7)  | 0.0056 (7)  | 0.0053 (7)  |
| C17 | 0.0550 (13) | 0.0229 (9)  | 0.0374 (10) | −0.0008 (8) | 0.0026 (9)  | 0.0069 (8)  |
| O11 | 0.0527 (8)  | 0.0372 (7)  | 0.0221 (6)  | 0.0057 (6)  | 0.0073 (6)  | 0.0043 (5)  |
| C21 | 0.0604 (15) | 0.0522 (13) | 0.0762 (16) | 0.0160 (11) | 0.0178 (13) | 0.0477 (13) |
| C22 | 0.0325 (9)  | 0.0459 (11) | 0.0341 (9)  | 0.0083 (8)  | 0.0003 (7)  | 0.0210 (9)  |
| O21 | 0.0336 (6)  | 0.0315 (6)  | 0.0238 (5)  | 0.0115 (5)  | 0.0080 (5)  | 0.0128 (5)  |

*Geometric parameters (Å, °)*

|                                        |             |               |             |
|----------------------------------------|-------------|---------------|-------------|
| Mn1—N1 <sup>i</sup>                    | 2.1543 (15) | C14—C15       | 1.385 (2)   |
| Mn1—N1                                 | 2.1543 (15) | C14—H14       | 0.9500      |
| Mn1—O21 <sup>i</sup>                   | 2.1928 (12) | C15—H15       | 0.9500      |
| Mn1—O21                                | 2.1929 (12) | C16—O11       | 1.219 (2)   |
| Mn1—N11 <sup>i</sup>                   | 2.3508 (14) | C16—C17       | 1.484 (3)   |
| Mn1—N11                                | 2.3508 (14) | C17—H17A      | 0.9800      |
| N1—C1                                  | 1.157 (2)   | C17—H17B      | 0.9800      |
| C1—S1                                  | 1.6211 (18) | C17—H17C      | 0.9800      |
| N11—C11                                | 1.334 (2)   | C21—C22       | 1.502 (3)   |
| N11—C15                                | 1.346 (2)   | C21—H21A      | 0.9800      |
| C11—C12                                | 1.383 (2)   | C21—H21B      | 0.9800      |
| C11—H11                                | 0.9500      | C21—H21C      | 0.9800      |
| C12—C13                                | 1.386 (2)   | C22—O21       | 1.435 (2)   |
| C12—H12                                | 0.9500      | C22—H22A      | 0.9900      |
| C13—C14                                | 1.381 (3)   | C22—H22B      | 0.9900      |
| C13—C16                                | 1.505 (2)   | O21—H1O1      | 0.8400      |
|                                        |             |               |             |
| N1 <sup>i</sup> —Mn1—N1                | 180.0       | C13—C14—H14   | 120.2       |
| N1 <sup>i</sup> —Mn1—O21 <sup>i</sup>  | 88.59 (5)   | C15—C14—H14   | 120.2       |
| N1—Mn1—O21 <sup>i</sup>                | 91.41 (5)   | N11—C15—C14   | 123.05 (16) |
| N1 <sup>i</sup> —Mn1—O21               | 91.41 (5)   | N11—C15—H15   | 118.5       |
| N1—Mn1—O21                             | 88.59 (5)   | C14—C15—H15   | 118.5       |
| O21 <sup>i</sup> —Mn1—O21              | 180.0       | O11—C16—C17   | 122.10 (16) |
| N1 <sup>i</sup> —Mn1—N11 <sup>i</sup>  | 91.13 (5)   | O11—C16—C13   | 118.40 (17) |
| N1—Mn1—N11 <sup>i</sup>                | 88.87 (5)   | C17—C16—C13   | 119.49 (16) |
| O21 <sup>i</sup> —Mn1—N11 <sup>i</sup> | 92.35 (5)   | C16—C17—H17A  | 109.5       |
| O21—Mn1—N11 <sup>i</sup>               | 87.65 (5)   | C16—C17—H17B  | 109.5       |
| N1 <sup>i</sup> —Mn1—N11               | 88.87 (5)   | H17A—C17—H17B | 109.5       |
| N1—Mn1—N11                             | 91.13 (5)   | C16—C17—H17C  | 109.5       |
| O21 <sup>i</sup> —Mn1—N11              | 87.65 (5)   | H17A—C17—H17C | 109.5       |
| O21—Mn1—N11                            | 92.35 (5)   | H17B—C17—H17C | 109.5       |
| N11 <sup>i</sup> —Mn1—N11              | 180.0       | C22—C21—H21A  | 109.5       |
| C1—N1—Mn1                              | 164.93 (13) | C22—C21—H21B  | 109.5       |
| N1—C1—S1                               | 178.67 (16) | H21A—C21—H21B | 109.5       |
| C11—N11—C15                            | 116.73 (14) | C22—C21—H21C  | 109.5       |

|             |             |               |             |
|-------------|-------------|---------------|-------------|
| C11—N11—Mn1 | 121.49 (11) | H21A—C21—H21C | 109.5       |
| C15—N11—Mn1 | 121.25 (11) | H21B—C21—H21C | 109.5       |
| N11—C11—C12 | 123.87 (16) | O21—C22—C21   | 112.19 (18) |
| N11—C11—H11 | 118.1       | O21—C22—H22A  | 109.2       |
| C12—C11—H11 | 118.1       | C21—C22—H22A  | 109.2       |
| C11—C12—C13 | 118.96 (17) | O21—C22—H22B  | 109.2       |
| C11—C12—H12 | 120.5       | C21—C22—H22B  | 109.2       |
| C13—C12—H12 | 120.5       | H22A—C22—H22B | 107.9       |
| C14—C13—C12 | 117.87 (15) | C22—O21—Mn1   | 130.79 (11) |
| C14—C13—C16 | 119.69 (15) | C22—O21—H1O1  | 105.5       |
| C12—C13—C16 | 122.44 (16) | Mn1—O21—H1O1  | 120.2       |
| C13—C14—C15 | 119.50 (15) |               |             |

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

*Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )*

| $D-H\cdots A$                       | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------------------------|-------|-------------|-------------|---------------|
| O21—H1O1 $\cdots$ O11 <sup>ii</sup> | 0.84  | 1.95        | 2.7714 (17) | 164           |

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