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(Pyridino-15-crown-5-κ^5N,O,O',O'',O''')-bis(thiocyanato-κN)manganese(II)

Chengjuan Li, Zejing Feng, Dacheng Li* and Daqi Wang

School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, People's Republic of China
Correspondence e-mail: dougroup@163.com

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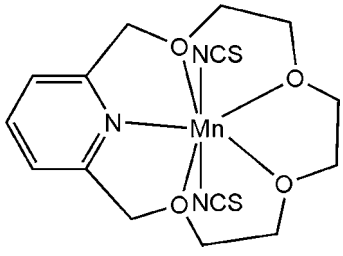
Key indicators: single-crystal X-ray study; T = 273 K; mean σ(C–C) = 0.006 Å; R factor = 0.044; wR factor = 0.113; data-to-parameter ratio = 15.4.

The title complex, $[Mn(NCS)_2(C_{13}H_{19}NO_4)]$ {systematic name: [3,6,9,12-tetraoxa-18-azabicyclo[12.3.1]octacosa-14(18),15,17-triene-κ^5N,O,O',O'',O''']bis(thiocyanato-κN)-manganese(II)}, was obtained by the reaction of $MnCl_2{\cdot}4H_2O$ and NaSCN with pyridino-15-crown-5. The Mn^{2+} center has a distorted pentagonal bipyramidal coordination geometry, coordinated by four O atoms and one N atom of the pyridino-15-crown-5 molecule, and by the N atoms of the two NCS^- ligands.

Related literature

For the coordination ability of pyridine crown ethers with transition metals, see: Lamb *et al.* (1980). For Mn—N(NCS) and Mn—O bond-length data, see: Wei *et al.* (1997).



Experimental

Crystal data

$[Mn(NCS)_2(C_{13}H_{19}NO_4)]$
M_r = 424.39
Monoclinic, $P2_1/c$
a = 15.211 (5) Å
b = 15.789 (5) Å
c = 7.868 (2) Å
β = 98.667 (4)°
V = 1868.0 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.95 mm^{-1}
T = 273 (2) K
0.42 × 0.35 × 0.31 mm

Data collection

Bruker SMART diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.690, T_{max} = 0.756
9681 measured reflections
3294 independent reflections
2266 reflections with $I > 2\sigma(I)$
R_{int} = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.113
S = 1.04
3294 reflections
214 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; 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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RN2037).

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supporting information

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(Pyridino-15-crown-5-κ^5N,O,O',O'',O''')bis(thiocyanato-κN)manganese(II)

Chengjuan Li, Zejing Feng, Dacheng Li and Daqi Wang

S1. Comment

The crown ethers, especially those containing one or more pyridine units have special coordination abilities with transition metal ions (Lamb *et al.*, 1980). To the best of our knowledge, this is the first crystal structure of the P15—C-5 complex. We report here the synthesis and structure of an Mn^{2+} complex with the P15—C-5 ligand. The title complex consists of one Mn^{2+} ion bound to one P15—C-5 and two NCS^- ligands. The Mn^{2+} ion is coordinated by four O atoms, one N atom of the P15—C-5 and two N atoms of the NCS^- ligands. The O1, O2, O3, O4, N1 atoms of the P15—C-5 crown ether are approximately co-planar and the two NCS^- ligands occupy the axial sites to form a distorted pentagonal bipyramid. Every O—Mn—O (or N) bond angle in the plane is nearly 72°, indicating that Mn^{2+} is situated at the center of the pentagon and the N,*O* atoms are located on the five corners. The average Mn—O [2.260 (3) Å] and Mn—N(NCS) [2.191 (3) Å] bond lengths are slightly bigger than the corresponding values in the complex [Mn(15—C-5)]$(SCN)_2$ [average 2.232 (5)Å and 2.130 (6) Å, respectively] (Wei *et al.*, 1997).

S2. Experimental

To a solution of pyridino-15-crown-5 (0.1265 g, 0.5 mmol) in 5 ml 1,2-dichloroethane was added 5 ml of an aqueous solution of $MnCl_2.4H_2O$ (0.394 g, 2 mmol) and NaSCN (0.80 g, 1 mmol). The mixture was stirred for 2 hrs at room temperature and then separated. Single crystals of (1) were obtained by evaporation of the substrate (m.p. 447–449 K). Analysis calculated for $C_{15}H_{19}MnN_3O_4S_2$: C 42.45, H 4.48, N 9.91%; found: C 42.39, H 4.38, N 10.10%.

S3. Refinement

All H atoms were positioned geometrically and treated as riding on their parent atoms, with C—H = 0.97 Å (aromatic) or 0.97Å (methylene) and $U_{iso}(H) = 1.2U_{eq}(C)$.

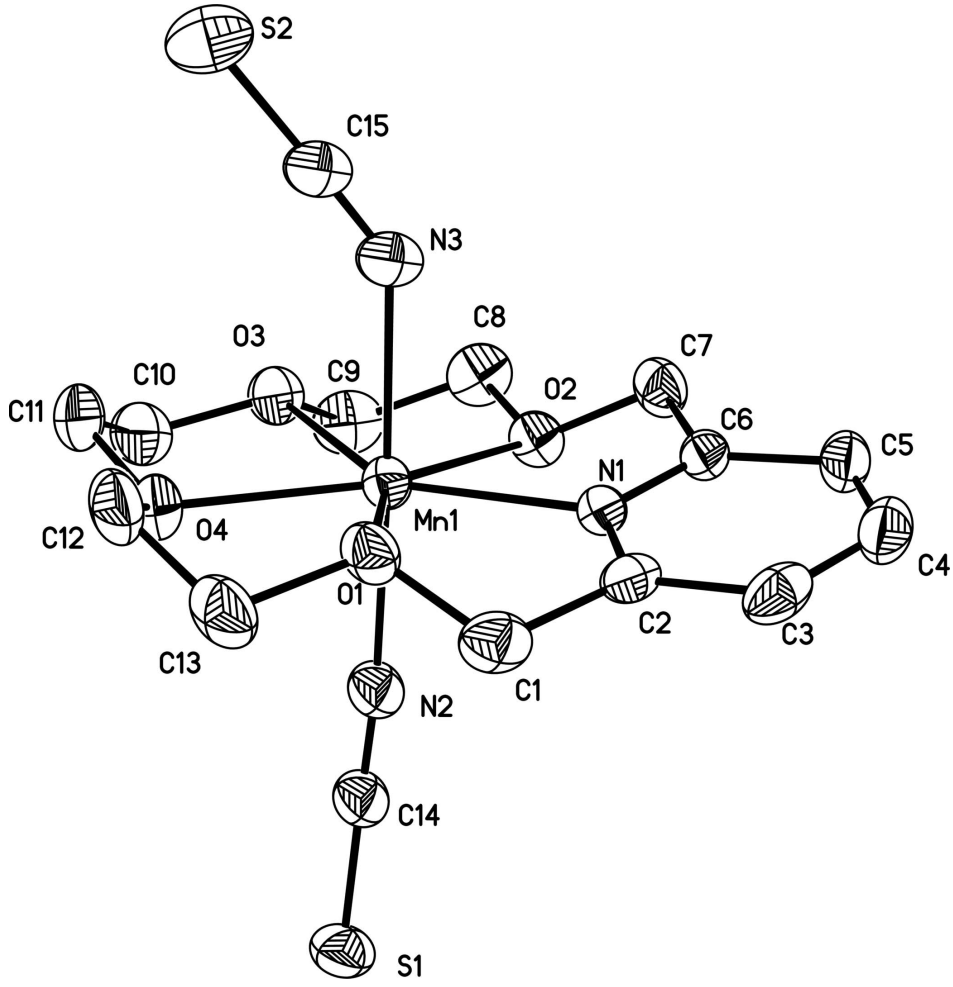

Figure 1

The molecular structure of (I), with atom labels and 30% probability displacement ellipsoids for non-H atoms.

[3,6,9,12-tetraoxa-18-azabicyclo[12.3.1]octacosa- 14 (18),15,17-triene-κ^5N,O,O',O'',O''']bis(thiocyanato-κN)manganese(II)

Crystal data

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$c = 7.868$ (2) Å
$\beta = 98.667$ (4)°
$V = 1868.0$ (10) Å^3
$Z = 4$
$F(000) = 876$
$D_x = 1.509$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2838 reflections
$\theta = 2.6$–23.5°
$\mu = 0.95$ mm^{-1}
$T = 273$ K
Block, colorless
0.42 × 0.35 × 0.31 mm

Data collection

Bruker SMART diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans

Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.690, T_{max} = 0.756
9681 measured reflections
3294 independent reflections
2266 reflections with $I > 2\sigma(I)$

R_{int} = 0.035
θ_{max} = 25.0°, θ_{min} = 1.9°
h = −15→18
k = −18→18
l = −9→8

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.113
S = 1.04
3294 reflections
214 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2 + 2.3622P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
Mn1	0.74410 (4)	0.96629 (4)	0.17191 (7)	0.04475 (19)
S1	0.51780 (7)	0.82256 (8)	0.45275 (15)	0.0685 (3)
S2	0.85210 (10)	1.19638 (8)	−0.11436 (17)	0.0796 (4)
N1	0.85451 (18)	0.92824 (19)	0.3697 (4)	0.0412 (7)
N2	0.6473 (2)	0.8938 (2)	0.2869 (4)	0.0575 (7)
N3	0.8384 (2)	1.0415 (2)	0.0450 (4)	0.0566 (7)
O1	0.75950 (17)	1.06277 (16)	0.3868 (3)	0.0526 (7)
O2	0.80310 (17)	0.84282 (16)	0.0915 (3)	0.0516 (7)
O3	0.68245 (17)	0.94099 (19)	−0.1028 (3)	0.0591 (7)
O4	0.63527 (17)	1.06201 (18)	0.1082 (4)	0.0622 (8)
C1	0.7964 (3)	1.0295 (3)	0.5502 (5)	0.0608 (11)
H1A	0.7503	1.0027	0.6042	0.073*
H1B	0.8227	1.0747	0.6245	0.073*
C2	0.8661 (2)	0.9658 (2)	0.5227 (4)	0.0459 (9)
C3	0.9378 (3)	0.9460 (3)	0.6468 (5)	0.0596 (11)
H3	0.9451	0.9719	0.7542	0.072*
C4	0.9980 (3)	0.8868 (3)	0.6068 (6)	0.0661 (12)
H4	1.0468	0.8725	0.6877	0.079*
C5	0.9863 (3)	0.8492 (3)	0.4484 (5)	0.0576 (11)

H5	1.0270	0.8096	0.4201	0.069*
C6	0.9129 (2)	0.8712 (2)	0.3317 (5)	0.0440 (9)
C7	0.8949 (3)	0.8344 (3)	0.1544 (5)	0.0577 (11)
H7A	0.9296	0.8640	0.0793	0.069*
H7B	0.9116	0.7751	0.1575	0.069*
C8	0.7770 (3)	0.8223 (3)	−0.0868 (5)	0.0674 (12)
H8A	0.7808	0.7617	−0.1040	0.081*
H8B	0.8157	0.8504	−0.1564	0.081*
C9	0.6835 (3)	0.8517 (3)	−0.1365 (6)	0.0748 (14)
H9A	0.6635	0.8406	−0.2574	0.090*
H9B	0.6444	0.8222	−0.0697	0.090*
C10	0.5985 (3)	0.9822 (4)	−0.1445 (6)	0.0759 (14)
H10A	0.5533	0.9520	−0.0940	0.091*
H10B	0.5808	0.9839	−0.2682	0.091*
C11	0.6091 (3)	1.0704 (3)	−0.0733 (6)	0.0761 (14)
H11A	0.6541	1.1009	−0.1240	0.091*
H11B	0.5534	1.1012	−0.0979	0.091*
C12	0.6526 (3)	1.1394 (3)	0.2025 (6)	0.0741 (13)
H12A	0.5991	1.1736	0.1927	0.089*
H12B	0.6985	1.1716	0.1582	0.089*
C13	0.6826 (3)	1.1154 (3)	0.3863 (6)	0.0703 (13)
H13A	0.6976	1.1655	0.4559	0.084*
H13B	0.6361	1.0847	0.4319	0.084*
C14	0.5933 (3)	0.8648 (3)	0.3547 (5)	0.0575 (7)
C15	0.8454 (3)	1.1064 (3)	−0.0202 (5)	0.0566 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0393 (3)	0.0494 (4)	0.0448 (3)	0.0020 (3)	0.0038 (2)	0.0014 (3)
S1	0.0508 (6)	0.0893 (9)	0.0677 (7)	−0.0094 (6)	0.0163 (5)	0.0039 (6)
S2	0.1000 (10)	0.0599 (8)	0.0809 (9)	−0.0263 (7)	0.0198 (7)	−0.0050 (6)
N1	0.0364 (16)	0.0466 (18)	0.0405 (17)	−0.0005 (14)	0.0049 (13)	0.0040 (14)
N2	0.0462 (17)	0.0603 (18)	0.0659 (18)	−0.0026 (13)	0.0079 (13)	0.0037 (13)
N3	0.0511 (14)	0.075 (2)	0.0435 (15)	−0.0143 (15)	0.0065 (12)	−0.0042 (13)
O1	0.0518 (16)	0.0525 (16)	0.0554 (16)	0.0106 (13)	0.0145 (13)	−0.0077 (13)
O2	0.0526 (16)	0.0547 (16)	0.0474 (15)	0.0010 (13)	0.0069 (12)	−0.0103 (12)
O3	0.0454 (16)	0.076 (2)	0.0520 (16)	−0.0081 (14)	−0.0062 (12)	0.0020 (14)
O4	0.0485 (16)	0.0656 (19)	0.0708 (19)	0.0135 (14)	0.0037 (14)	0.0110 (15)
C1	0.068 (3)	0.073 (3)	0.043 (2)	−0.004 (2)	0.013 (2)	−0.008 (2)
C2	0.050 (2)	0.051 (2)	0.0370 (19)	−0.0083 (18)	0.0083 (17)	0.0059 (17)
C3	0.067 (3)	0.067 (3)	0.041 (2)	−0.024 (2)	−0.005 (2)	0.0091 (19)
C4	0.048 (2)	0.070 (3)	0.074 (3)	−0.010 (2)	−0.010 (2)	0.029 (2)
C5	0.046 (2)	0.056 (3)	0.068 (3)	0.0039 (19)	0.001 (2)	0.018 (2)
C6	0.040 (2)	0.040 (2)	0.052 (2)	−0.0001 (17)	0.0067 (17)	0.0092 (17)
C7	0.053 (3)	0.057 (3)	0.064 (3)	0.014 (2)	0.014 (2)	−0.004 (2)
C8	0.084 (3)	0.064 (3)	0.054 (3)	−0.004 (2)	0.008 (2)	−0.018 (2)
C9	0.080 (3)	0.086 (4)	0.054 (3)	−0.026 (3)	−0.004 (2)	−0.018 (2)

C10	0.047 (3)	0.116 (4)	0.059 (3)	−0.006 (3)	−0.010 (2)	0.011 (3)
C11	0.047 (3)	0.100 (4)	0.077 (3)	0.016 (3)	−0.004 (2)	0.030 (3)
C12	0.061 (3)	0.060 (3)	0.103 (4)	0.026 (2)	0.018 (3)	0.008 (3)
C13	0.068 (3)	0.061 (3)	0.086 (3)	0.018 (2)	0.027 (3)	−0.012 (2)
C14	0.0462 (17)	0.0603 (18)	0.0659 (18)	−0.0026 (13)	0.0079 (13)	0.0037 (13)
C15	0.0511 (14)	0.075 (2)	0.0435 (15)	−0.0143 (15)	0.0065 (12)	−0.0042 (13)

Geometric parameters (Å, º)

Mn1—N2	2.168 (3)	C3—C4	1.377 (6)
Mn1—N1	2.195 (3)	C3—H3	0.9300
Mn1—N3	2.213 (3)	C4—C5	1.368 (6)
Mn1—O4	2.242 (3)	C4—H4	0.9300
Mn1—O3	2.259 (3)	C5—C6	1.380 (5)
Mn1—O1	2.262 (3)	C5—H5	0.9300
Mn1—O2	2.276 (3)	C6—C7	1.497 (5)
S1—C14	1.620 (4)	C7—H7A	0.9700
S2—C15	1.612 (5)	C7—H7B	0.9700
N1—C2	1.329 (4)	C8—C9	1.490 (6)
N1—C6	1.330 (4)	C8—H8A	0.9700
N2—C14	1.140 (5)	C8—H8B	0.9700
N3—C15	1.158 (5)	C9—H9A	0.9700
O1—C1	1.423 (5)	C9—H9B	0.9700
O1—C13	1.433 (5)	C10—C11	1.501 (7)
O2—C7	1.415 (4)	C10—H10A	0.9700
O2—C8	1.436 (5)	C10—H10B	0.9700
O3—C10	1.426 (5)	C11—H11A	0.9700
O3—C9	1.435 (5)	C11—H11B	0.9700
O4—C11	1.430 (5)	C12—C13	1.498 (6)
O4—C12	1.433 (5)	C12—H12A	0.9700
C1—C2	1.500 (5)	C12—H12B	0.9700
C1—H1A	0.9700	C13—H13A	0.9700
C1—H1B	0.9700	C13—H13B	0.9700
C2—C3	1.386 (5)		

N2—Mn1—N1	93.15 (12)	C3—C4—H4	119.9
N2—Mn1—N3	177.51 (12)	C4—C5—C6	118.6 (4)
N1—Mn1—N3	89.32 (12)	C4—C5—H5	120.7
N2—Mn1—O4	85.63 (12)	C6—C5—H5	120.7
N1—Mn1—O4	143.47 (11)	N1—C6—C5	121.4 (4)
N3—Mn1—O4	92.55 (12)	N1—C6—C7	116.0 (3)
N2—Mn1—O3	95.50 (11)	C5—C6—C7	122.6 (4)
N1—Mn1—O3	142.50 (11)	O2—C7—C6	108.8 (3)
N3—Mn1—O3	82.35 (11)	O2—C7—H7A	109.9
O4—Mn1—O3	73.69 (11)	C6—C7—H7A	109.9
N2—Mn1—O1	92.52 (12)	O2—C7—H7B	109.9
N1—Mn1—O1	70.86 (10)	C6—C7—H7B	109.9
N3—Mn1—O1	88.56 (11)	H7A—C7—H7B	108.3

O4—Mn1—O1	72.72 (10)	O2—C8—C9	107.4 (3)
O3—Mn1—O1	144.69 (10)	O2—C8—H8A	110.2
N2—Mn1—O2	89.15 (11)	C9—C8—H8A	110.2
N1—Mn1—O2	70.79 (10)	O2—C8—H8B	110.2
N3—Mn1—O2	91.40 (12)	C9—C8—H8B	110.2
O4—Mn1—O2	145.52 (10)	H8A—C8—H8B	108.5
O3—Mn1—O2	72.93 (10)	O3—C9—C8	107.1 (3)
O1—Mn1—O2	141.65 (9)	O3—C9—H9A	110.3
C2—N1—C6	120.2 (3)	C8—C9—H9A	110.3
C2—N1—Mn1	120.2 (2)	O3—C9—H9B	110.3
C6—N1—Mn1	119.4 (2)	C8—C9—H9B	110.3
C14—N2—Mn1	171.8 (3)	H9A—C9—H9B	108.5
C15—N3—Mn1	141.6 (3)	O3—C10—C11	107.2 (3)
C1—O1—C13	115.3 (3)	O3—C10—H10A	110.3
C1—O1—Mn1	114.1 (2)	C11—C10—H10A	110.3
C13—O1—Mn1	113.3 (2)	O3—C10—H10B	110.3
C7—O2—C8	115.7 (3)	C11—C10—H10B	110.3
C7—O2—Mn1	113.1 (2)	H10A—C10—H10B	108.5
C8—O2—Mn1	113.7 (2)	O4—C11—C10	106.5 (4)
C10—O3—C9	116.1 (3)	O4—C11—H11A	110.4
C10—O3—Mn1	111.6 (3)	C10—C11—H11A	110.4
C9—O3—Mn1	109.6 (2)	O4—C11—H11B	110.4
C11—O4—C12	116.1 (4)	C10—C11—H11B	110.4
C11—O4—Mn1	111.8 (3)	H11A—C11—H11B	108.6
C12—O4—Mn1	112.8 (2)	O4—C12—C13	106.8 (4)
O1—C1—C2	108.0 (3)	O4—C12—H12A	110.4
O1—C1—H1A	110.1	C13—C12—H12A	110.4
C2—C1—H1A	110.1	O4—C12—H12B	110.4
O1—C1—H1B	110.1	C13—C12—H12B	110.4
C2—C1—H1B	110.1	H12A—C12—H12B	108.6
H1A—C1—H1B	108.4	O1—C13—C12	106.2 (3)
N1—C2—C3	121.4 (4)	O1—C13—H13A	110.5
N1—C2—C1	115.4 (3)	C12—C13—H13A	110.5
C3—C2—C1	123.2 (4)	O1—C13—H13B	110.5
C4—C3—C2	118.1 (4)	C12—C13—H13B	110.5
C4—C3—H3	120.9	H13A—C13—H13B	108.7
C2—C3—H3	120.9	N2—C14—S1	179.1 (4)
C5—C4—C3	120.3 (4)	N3—C15—S2	178.3 (4)
C5—C4—H4	119.9		