

**(Pyridino-15-crown-5- $\kappa^5N,O,O',O'',O'''$ )-bis(thiocyanato- $\kappa N$ )manganese(II)**

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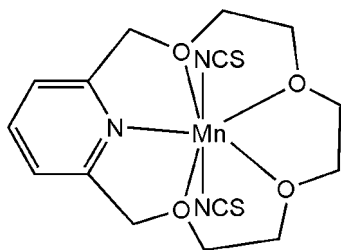
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Key indicators: single-crystal X-ray study;  $T = 273$  K; mean  $\sigma(C-C) = 0.006$  Å;  $R$  factor = 0.044;  $wR$  factor = 0.113; data-to-parameter ratio = 15.4.

The title complex,  $[Mn(NCS)_2(C_{13}H_{19}NO_4)]$  {systematic name: [3,6,9,12-tetraoxa-18-azabicyclo[12.3.1]octacos-14(18),15,17-triene- $\kappa^5N,O,O',O'',O'''$ ]bis(thiocyanato- $\kappa N$ )-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  
 $\beta = 98.667$  (4)°

$V = 1868.0$  (10) Å<sup>3</sup>  
 $Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 0.95$  mm<sup>-1</sup>  
 $T = 273$  (2) K  
 $0.42 \times 0.35 \times 0.31$  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<sup>-3</sup>  
 $\Delta\rho_{min} = -0.47$  e Å<sup>-3</sup>

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).

**References**

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**supplementary materials**

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## (Pyridino-15-crown-5- $\kappa^5N,O,O',O'',O'''$ )bis(thiocyanato- $\kappa N$ )manganese(II)

C. Li, Z. Feng, D. Li and D. Wang

### 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  $72^\circ$ , 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).

### 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  $MnCl_2 \cdot 4H_2O$  (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%.

### Refinement

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

### Figures

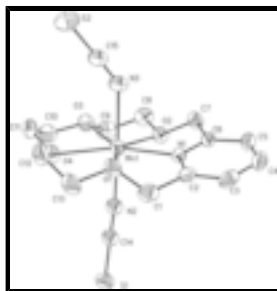


Fig. 1. The molecular structure of (I), with atom labels and 30% probability displacement ellipsoids for non-H atoms.

# supplementary materials

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## [3,6,9,12-tetraoxa-18-azabicyclo[12.3.1]octacos-14 (18),15,17-triene- $\kappa^5$ N,O,O',O'',O''']bis(thiocyanato- $\kappa$ N)manganese(II)

### Crystal data

[Mn(NCS) <sub>2</sub> (C <sub>13</sub> H <sub>19</sub> NO <sub>4</sub> )]	$F_{000} = 876$
$M_r = 424.39$	$D_x = 1.509 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 15.211 (5) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$b = 15.789 (5) \text{ \AA}$	Cell parameters from 2838 reflections
$c = 7.868 (2) \text{ \AA}$	$\theta = 2.6\text{--}23.5^\circ$
$\beta = 98.667 (4)^\circ$	$\mu = 0.95 \text{ mm}^{-1}$
$V = 1868.0 (10) \text{ \AA}^3$	$T = 273 (2) \text{ K}$
$Z = 4$	Block, colorless
	$0.42 \times 0.35 \times 0.31 \text{ mm}$

### Data collection

Bruker SMART diffractometer	3294 independent reflections
Radiation source: fine-focus sealed tube	2266 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.035$
$T = 273(2) \text{ K}$	$\theta_{\text{max}} = 25.0^\circ$
$\varphi$ and $\omega$ scans	$\theta_{\text{min}} = 1.9^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -15 \rightarrow 18$
$T_{\text{min}} = 0.690, T_{\text{max}} = 0.756$	$k = -18 \rightarrow 18$
9681 measured reflections	$l = -9 \rightarrow 8$

### Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.043$	H-atom parameters constrained
$wR(F^2) = 0.113$	$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2 + 2.3622P]$
$S = 1.04$	where $P = (F_o^2 + 2F_c^2)/3$
3294 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
214 parameters	$\Delta\rho_{\text{max}} = 0.63 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-3}$
	Extinction correction: none

*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  $F^2 > 2\sigma(F^2)$  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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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*

## supplementary materials

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
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 ( $\text{\AA}$ , $^\circ$ )

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

## supplementary materials

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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		



Fig. 1

