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Bis{3-[(*E*)-2-(aminocarbonyl)hydrazonomethyl]pyridine}diaquadiisothiocyanatomanganese(II)

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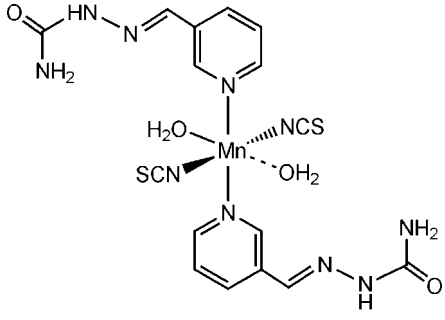
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å; R factor = 0.040; wR factor = 0.116; data-to-parameter ratio = 18.1.

In the title complex, $[Mn(SCN)_2(H\text{-}Pysc)_2(H_2O)_2]$ {H-Pysc = 3-[2-(aminocarbonyl)hydrazonomethyl]pyridine, $C_7H_8N_4O$}, Mn^{II}, located at an inversion centre, is coordinated by two thiocyanate anions, two water molecules and two molecules of the neutral Schiff base ligand H-Pysc, forming an octahedral configuration. The Schiff base acts as a monodentate ligand, coordinating to the metal through the pyridyl N atom, whereas the amide O and imine N atoms remain uncoordinated. The complex molecules are held together by intermolecular hydrogen bonds into a three-dimensional supramolecular network.

Related literature

For related literature, see: Beraldo *et al.* (2001); Chen, Zhou, Li *et al.* (2004); Chen, Zhou, Liang *et al.* (2004).



Experimental

Crystal data

$[Mn(SCN)_2(C_7H_8N_4O)_2(H_2O)_2]$
M_r = 535.48
Triclinic, $P\overline{1}$
a = 6.6998 (19) Å
b = 9.329 (3) Å
c = 10.478 (3) Å
α = 64.770 (3)°
β = 82.711 (3)°
γ = 75.384 (3)°
V = 573.1 (3) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.80 mm^{-1}
T = 173 (2) K
0.56 × 0.46 × 0.35 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.647, T_{max} = 0.753
5162 measured reflections
2738 independent reflections
2010 reflections with $I > 2\sigma(I)$
R_{int} = 0.068

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.116
S = 1.06
2738 reflections
151 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.61 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—N5	2.193 (2)	Mn1—N1	2.3085 (18)
Mn1—O1*W*	2.2203 (17)		
N5—Mn1—N5^{i}	180	O1*W*—Mn1—N1	89.52 (6)
N5—Mn1—O1*W*^{i}	88.84 (8)	N5—Mn1—N1^{i}	89.99 (7)
N5—Mn1—O1*W*	91.16 (8)	O1*W*—Mn1—N1^{i}	90.48 (6)
O1*W*^{i}—Mn1—O1*W*	180	N1—Mn1—N1^{i}	180
N5—Mn1—N1	90.01 (7)		

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*A*···O1^{ii}	0.84	1.90	2.724 (3)	164
O1*W*—H1*B*···S1^{iii}	0.85	2.52	3.352 (2)	164
N3—H3*A*···O1^{iv}	0.88	1.99	2.865 (3)	175
N4—H4*A*···N2	0.88	2.28	2.637 (3)	104

Symmetry codes: (ii) $x+1, y, z+1$; (iii) $-x, -y, -z$; (iv) $-x-1, -y, -z-1$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2108).

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supplementary materials

Acta Cryst. (2007). E**63**, m1747 [**doi:10.1107/S1600536807023707**]

Bis{3-[(*E*)-2-(aminocarbonyl)hydrazonomethyl]pyridine}diaquadiisothiocyanatomanganese(II)

D.-C. Zhong, G.-Q. Guo and J.-H. Deng

Comment

Structurally characterized metal-organic complexes based on the Schiff base ligands derived from semicarbazone have been reported due to their antimicrobial, cytotoxic and antioxidant activities (Chen, Zhou, Liang *et al.*, 2004; Chen, Zhou, Li *et al.*, 2004; Beraldo *et al.*, 2001). We report here the crystal structure of the title compound (I).

The Mn atom in compound (I) is six-coordinated by two O atoms of water molecules and four N atoms, two of which come from two thiocyanate anions and the rest from H-Pysc ligands (Fig. 1). The bond lengths and three *trans* angles at Mn1 suggests a slightly distorted octahedral geometry (Table 1).

The molecules are held together by intermolecular hydrogen bonding forming three-dimensional supramolecular network. The coordinated water molecules (O1W) donate H atoms to the terminal O1 atom and thiocyanate S atoms to form O—H···O^{i} and O—H···S^{ii} hydrogen bonds, respectively (Table 2, Fig. 2) The O1 atoms also accept H atom from N3 to form N—H···O^{iii} hydrogen bonds (Table 2, Fig. 2).

Experimental

1.0 mmol H-Pysc, 0.5 mmol $Mn(Ac)_2{\cdot}4H_2O$ and 1.0 mmol of $(NH_4)SCN$ were dissolved in a water-ethanol mixture (1:2 *v*/*v*; 20 ml), and the mixture was stirred for *ca* 2 h at 343 K. The mixture was further stirred for another 1 h at 333 K and filtered. The resultant filtrate was left to stand for slow evaporation at room temperature. Colourless single crystals of (I) suitable for X-ray structure analysis were obtained after a period of 15 days (yield 72%).

Refinement

Hydrogen atoms attached to carbon atoms and nitrogen atoms were positioned geometrically and treated as riding, with C—H = 0.93 Å, N—H = 0.86 Å, and U_{iso}(H) = 1.2U_{eq}(C or N)]. Water H atoms were located in difference maps and constrained to ride at O—H distances (0.85 Å) with U_{iso}(H) = 1.5U_{eq}(O).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(*s*) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(*s*) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

Figures

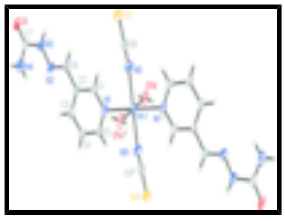

Fig. 1. The structure of (I) showing the 50% probability displacement ellipsoids and the atom-labelling scheme [symmetry code: (i) − *x* + 1, − *y*, - *z*.].

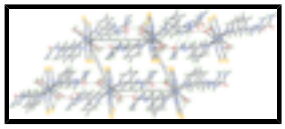

Fig. 2. Three-dimensional supramolecular network constructed by hydrogen bonds (dashed lines).

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Crystal data

$[Mn(SCN)_2(C_7H_8N_4O)_2(H_2O)_2]$	$Z = 1$
$M_r = 535.48$	$F_{000} = 275$
Triclinic, $P\overline{1}$	$D_x = 1.551$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 6.6998$ (19) Å	Cell parameters from 2857 reflections
$b = 9.329$ (3) Å	$\theta = 2.2$–28.4°
$c = 10.478$ (3) Å	$\mu = 0.80$ mm^{-1}
$\alpha = 64.770$ (3)°	$T = 173$ (2) K
$\beta = 82.711$ (3)°	Block, colourless
$\gamma = 75.384$ (3)°	0.56 × 0.46 × 0.35 mm
$V = 573.1$ (3) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	2738 independent reflections
Radiation source: fine-focus sealed tube	2010 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.068$
$T = 173$(2) K	$\theta_{max} = 28.4^\circ$
phi and ω scans	$\theta_{min} = 2.2^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 1998)	$h = -8 \rightarrow 8$
$T_{min} = 0.647$, $T_{max} = 0.753$	$k = -12 \rightarrow 12$
5162 measured reflections	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.040$	H-atom parameters constrained
$wR(F^2) = 0.116$	$w = 1/[\sigma^2(F_o^2) + (0.0574P)^2 + 0.0195P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
2738 reflections	$\Delta\rho_{max} = 0.61$ e Å^{-3}
151 parameters	$\Delta\rho_{min} = -0.48$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0.5000	0.0000	0.0000	0.03568 (17)
S1	0.11296 (10)	−0.42537 (8)	0.10273 (8)	0.0535 (2)
O1	−0.5650 (3)	0.1500 (2)	−0.67672 (18)	0.0485 (4)
N2	−0.1690 (3)	0.1982 (2)	−0.5220 (2)	0.0377 (4)
O1W	0.2788 (3)	0.1500 (2)	0.09562 (18)	0.0509 (5)
H1B	0.1822	0.2316	0.0542	0.076*
H1A	0.3169	0.1696	0.1592	0.076*
N1	0.3320 (3)	0.1506 (2)	−0.21142 (19)	0.0347 (4)
C1	0.1792 (3)	0.1049 (3)	−0.2461 (2)	0.0347 (5)
H1	0.1338	0.0120	−0.1781	0.042*
C2	0.0843 (3)	0.1862 (3)	−0.3759 (2)	0.0327 (5)
N3	−0.3197 (3)	0.1331 (2)	−0.5403 (2)	0.0413 (5)
H3A	−0.3478	0.0434	−0.4733	0.050*
C8	0.2205 (3)	−0.2772 (3)	0.0791 (2)	0.0394 (5)
C3	0.1501 (3)	0.3210 (3)	−0.4753 (2)	0.0391 (5)
H3	0.0917	0.3774	−0.5663	0.047*
C6	−0.0808 (3)	0.1251 (3)	−0.4029 (2)	0.0377 (5)
H6	−0.1216	0.0317	−0.3321	0.045*
C5	0.3886 (3)	0.2840 (3)	−0.3076 (2)	0.0410 (5)
H5	0.4933	0.3205	−0.2842	0.049*
N5	0.2998 (3)	−0.1731 (3)	0.0611 (2)	0.0514 (5)
C7	−0.4251 (3)	0.2080 (3)	−0.6625 (3)	0.0410 (5)
C4	0.3025 (4)	0.3718 (3)	−0.4394 (3)	0.0481 (6)
H4	0.3479	0.4661	−0.5046	0.058*

N4	−0.3730 (4)	0.3407 (3)	−0.7595 (2)	0.0654 (7)
H4B	−0.4384	0.3936	−0.8398	0.078*
H4A	−0.2728	0.3762	−0.7438	0.078*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0336 (3)	0.0431 (3)	0.0360 (3)	−0.0139 (2)	−0.01144 (19)	−0.0156 (2)
S1	0.0500 (4)	0.0465 (4)	0.0689 (5)	−0.0199 (3)	−0.0100 (3)	−0.0207 (3)
O1	0.0491 (9)	0.0577 (11)	0.0472 (10)	−0.0107 (8)	−0.0229 (8)	−0.0242 (9)
N2	0.0311 (9)	0.0479 (11)	0.0422 (11)	−0.0095 (8)	−0.0094 (8)	−0.0232 (9)
O1W	0.0520 (10)	0.0606 (11)	0.0473 (10)	−0.0018 (8)	−0.0200 (8)	−0.0298 (9)
N1	0.0306 (8)	0.0422 (10)	0.0369 (10)	−0.0084 (7)	−0.0099 (7)	−0.0188 (8)
C1	0.0311 (10)	0.0422 (12)	0.0344 (11)	−0.0119 (9)	−0.0062 (9)	−0.0156 (10)
C2	0.0246 (9)	0.0439 (12)	0.0351 (11)	−0.0067 (8)	−0.0057 (8)	−0.0205 (10)
N3	0.0385 (10)	0.0475 (11)	0.0434 (11)	−0.0132 (8)	−0.0183 (8)	−0.0170 (9)
C8	0.0354 (11)	0.0468 (13)	0.0368 (12)	−0.0107 (9)	−0.0125 (9)	−0.0139 (10)
C3	0.0329 (10)	0.0501 (13)	0.0353 (12)	−0.0093 (10)	−0.0095 (9)	−0.0159 (10)
C6	0.0321 (10)	0.0447 (12)	0.0398 (13)	−0.0101 (9)	−0.0104 (9)	−0.0172 (10)
C5	0.0347 (11)	0.0498 (13)	0.0443 (14)	−0.0171 (10)	−0.0101 (10)	−0.0180 (11)
N5	0.0496 (12)	0.0577 (13)	0.0519 (13)	−0.0251 (10)	−0.0142 (10)	−0.0165 (11)
C7	0.0404 (11)	0.0497 (13)	0.0396 (13)	−0.0062 (10)	−0.0142 (10)	−0.0231 (11)
C4	0.0434 (12)	0.0522 (15)	0.0461 (15)	−0.0229 (11)	−0.0109 (11)	−0.0083 (12)
N4	0.0730 (16)	0.0786 (17)	0.0439 (13)	−0.0333 (14)	−0.0224 (12)	−0.0097 (12)

Geometric parameters (Å, °)

Mn1—N5	2.193 (2)	C1—H1	0.9500
Mn1—N5^{i}	2.193 (2)	C2—C3	1.381 (3)
Mn1—O1W^{i}	2.2203 (17)	C2—C6	1.471 (3)
Mn1—O1W	2.2203 (17)	N3—C7	1.358 (3)
Mn1—N1	2.3085 (18)	N3—H3A	0.8800
Mn1—N1^{i}	2.3085 (18)	C8—N5	1.158 (3)
S1—C8	1.630 (2)	C3—C4	1.380 (3)
O1—C7	1.246 (3)	C3—H3	0.9500
N2—C6	1.276 (3)	C6—H6	0.9500
N2—N3	1.372 (2)	C5—C4	1.383 (3)
O1W—H1B	0.8533	C5—H5	0.9500
O1W—H1A	0.8447	C7—N4	1.320 (3)
N1—C5	1.335 (3)	C4—H4	0.9500
N1—C1	1.345 (2)	N4—H4B	0.8800
C1—C2	1.387 (3)	N4—H4A	0.8800
N5—Mn1—N5^{i}	180.00 (9)	C3—C2—C6	122.49 (19)
N5—Mn1—O1W^{i}	88.84 (8)	C1—C2—C6	119.0 (2)
N5^{i}—Mn1—O1W^{i}	91.16 (8)	C7—N3—N2	119.6 (2)
N5—Mn1—O1W	91.16 (8)	C7—N3—H3A	120.2
N5^{i}—Mn1—O1W	88.84 (8)	N2—N3—H3A	120.2

O1W^{i}—Mn1—O1W	180.00 (13)	N5—C8—S1	178.8 (2)
N5—Mn1—N1	90.01 (7)	C4—C3—C2	118.5 (2)
N5^{i}—Mn1—N1	89.99 (7)	C4—C3—H3	120.8
O1W^{i}—Mn1—N1	90.48 (6)	C2—C3—H3	120.8
O1W—Mn1—N1	89.52 (6)	N2—C6—C2	119.7 (2)
N5—Mn1—N1^{i}	89.99 (7)	N2—C6—H6	120.1
N5^{i}—Mn1—N1^{i}	90.01 (7)	C2—C6—H6	120.1
O1W^{i}—Mn1—N1^{i}	89.52 (6)	N1—C5—C4	123.3 (2)
O1W—Mn1—N1^{i}	90.48 (6)	N1—C5—H5	118.4
N1—Mn1—N1^{i}	180.00 (6)	C4—C5—H5	118.4
C6—N2—N3	116.5 (2)	C8—N5—Mn1	167.3 (2)
Mn1—O1W—H1B	127.1	O1—C7—N4	123.9 (2)
Mn1—O1W—H1A	120.4	O1—C7—N3	119.1 (2)
H1B—O1W—H1A	104.6	N4—C7—N3	117.1 (2)
C5—N1—C1	116.89 (18)	C3—C4—C5	119.3 (2)
C5—N1—Mn1	121.13 (13)	C3—C4—H4	120.4
C1—N1—Mn1	121.93 (15)	C5—C4—H4	120.4
N1—C1—C2	123.5 (2)	C7—N4—H4B	120.0
N1—C1—H1	118.2	C7—N4—H4A	120.0
C2—C1—H1	118.2	H4B—N4—H4A	120.0
C3—C2—C1	118.52 (19)		

Symmetry codes: (i) −*x*+1, −*y*, −*z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H1A···O1^{ii}	0.84	1.90	2.724 (3)	164
O1W—H1B···S1^{iii}	0.85	2.52	3.352 (2)	164
N3—H3A···O1^{iv}	0.88	1.99	2.865 (3)	175
N4—H4A···N2	0.88	2.28	2.637 (3)	104

Symmetry codes: (ii) *x*+1, *y*, *z*+1; (iii) −*x*, −*y*, −*z*; (iv) −*x*−1, −*y*, −*z*−1.

Fig. 1

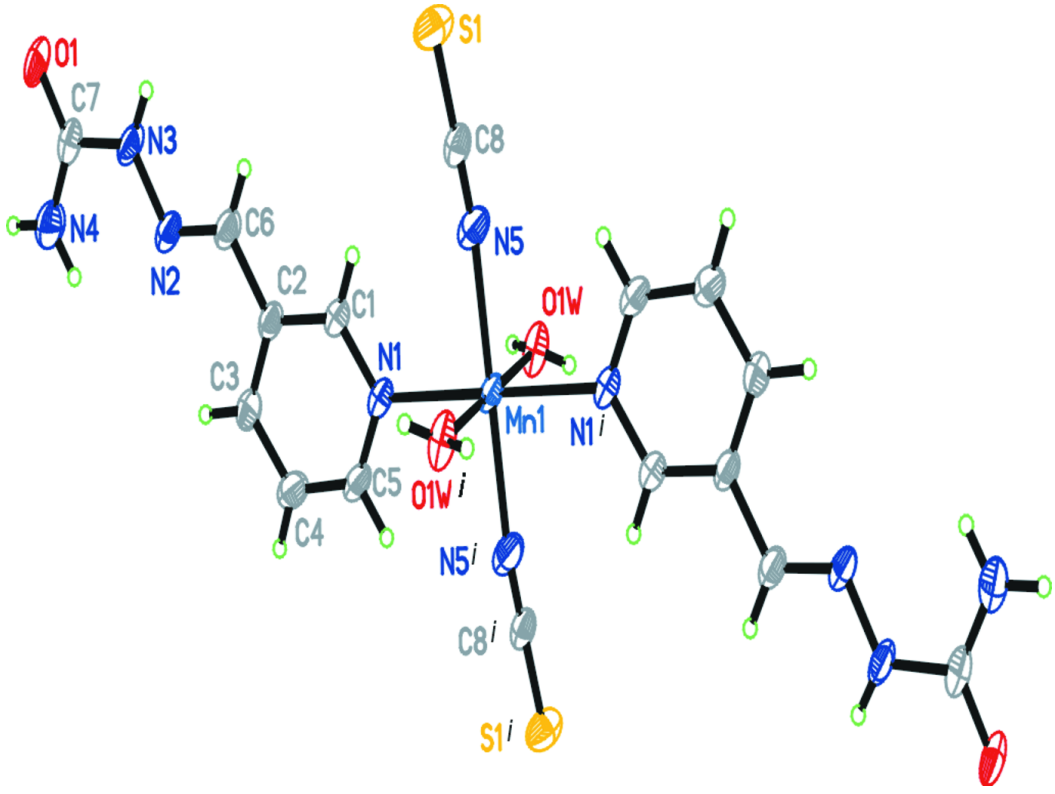
S1
O1
C7
C8
N3
N5
N4
C6
N2
C2
C1
O1W
N1
C3
Mn1
N1i
O1Wi
C5
C4
N5i
C8i
S1i

Fig. 2