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Bis[1-(pyridin-2-yl)ethanone-κN 4-phenylthiosemicarbazonato-κ^2N^4,S]manganese(II)

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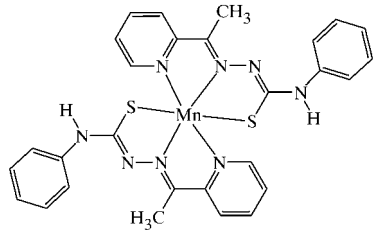
One half of the molecule of the title complex, $[Mn(C_{14}H_{13}N_4S)_2]$, is related to the other half by a twofold axis passing through the Mn atom. This high-spin Mn atom is six-coordinated, in an octahedral geometry, by the azomethine N, the pyridyl N and the thiolate S atom of two planar 1-(pyridin-2-yl)ethanone *N*(4)-phenylthiosemicarbazone ligands. In the crystal, the molecules are interconnected by N—H···S and C—H···N interactions, forming a three-dimensional network.

Comment

The formation of complexes with transition metal ions has been proposed as a step in increasing the biological activity of certain thiosemicarbazones (West *et al.*, 1993). Metal complexes of thiosemicarbazones assume interesting structural geometries which may be crucial in deciding their biological activities. Recently, we have reported some biologically active heterocyclic base adducts of Cu^{II} (Bindu *et al.*, 1999), Ni^{II} (Bindu & Kurup, 1997) and Fe^{III} (Bindu & Kurup, 1999) complexes of salicylaldehyde thiosemicarbazones. 2-Acetylpyridine [or 1-(pyridin-2-yl)ethanone] thiosemicarbazones are the first thiosemicarbazones in which antimalarial activity was detected. The highest activity is reported when the N4 position is either disubstituted or is part of a ring system (Klayman *et al.*, 1979). Transition metal complexes of these thiosemicarbazones have also been screened for their medicinal properties (Scovill *et al.*, 1982) and were found to be more active than the ligands. Manganese complexes are of considerable interest because they can mimic the active sites of manganese-containing enzymes (Limburg *et al.*, 1999). Spectral studies of Mn^{II} complexes of *N*(4)-substituted 2-acetylpyridine thiosemicarbazone has been reported (Garg *et al.*, 1988), but their crystal structures have not yet been established. We have synthesized and crystallized Mn^{II} complexes of 2-acetylpyridine thiosemicarbazone in order to study systematically the relationship between the structural properties and biological activities. An X-ray crystal structure analysis of the title compound, bis[1-(pyridin-2-yl)ethanone 4-phenylthiosemicarbazonato]manganese(II), (I), was undertaken, and the results are reported here.



(I)

The title complex is an Mn^{II} complex of 2-acetylpyridine *N*(4)-phenylthiosemicarbazone, and the ligands coordinate as *N,N,S*-donors through the azomethine N, the pyridyl N and the thiolate S atom.

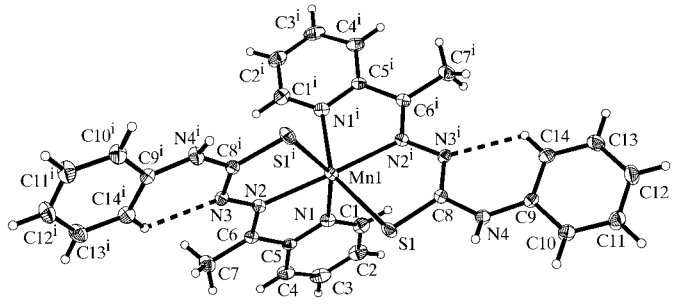


Figure 1
The structure of the title complex, showing 50% probability displacement ellipsoids and the atom-numbering scheme. The dashed lines denote intramolecular hydrogen bonds. [Symmetry code: (i) $-x, y, -z+\frac{3}{2}$.]

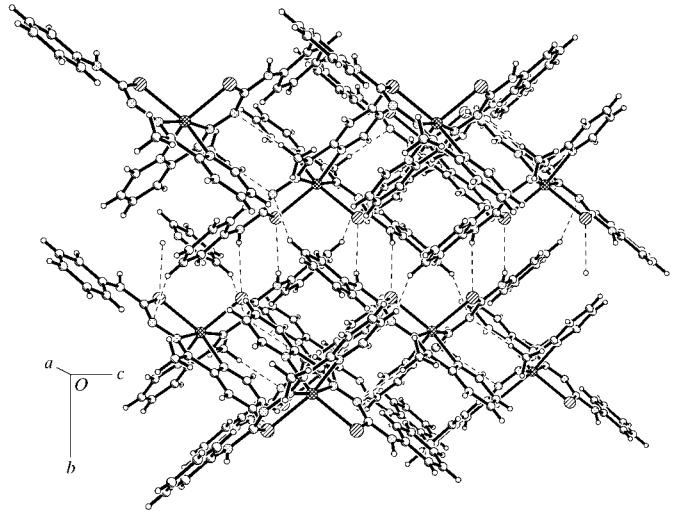


Figure 2
The packing structure of the title complex, viewed down the *a* axis, showing the three-dimensional network. The dashed lines denote intermolecular hydrogen bonds.

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The bond lengths and angles (Table 1) of the title complex (Fig. 1) are normal (Allen *et al.*, 1987). The asymmetric unit contains one half of the molecule, and the other half is generated by a twofold axis passing through atom Mn1, which is coordinated octahedrally by *N,N,S*-donors of the two deprotonated ligands. This structure is identical to the closely related Fe^{III} (West *et al.*, 1985) and Co^{III} (West *et al.*, 1986) complexes, where the two coordinating azomethine N atoms are *trans* to each other and the other two sets of identical donor atoms are *cis* to each other.

The apical positions of the octahedron are occupied by the azomethine N2 atoms, with an N2—Mn1—N2^{i} angle of 170.4 (1)° [symmetry code: (i) $-x, y, -z+\frac{3}{2}$]. The average angle of the apical N2 atom to the basal plane (N1/N1^{i}/S1/S1^{i}) subtended at atom Mn1 is 89.9°, while angles N1—Mn1—S1 and N1—Mn1—S1^{i} are 147.76 (6) and 91.44 (6)°, respectively.

As a result of the coordination, the thiosemicarbazone C8—S1 bond distance increases from 1.699 Å (Ferrari *et al.*, 1992) to 1.740 (3) Å in (I), and the C8—N3 bond distance decreases from 1.358 Å (Ferrari *et al.*, 1992) to 1.315 (3) Å. These bond distances are consistent with C8—S1 having partial single-bond and C8—N3 partial double-bond character. The comparatively longer bond lengths of Mn1—N1, Mn1—N2 and Mn1—S1 indicate weak coordination to the Mn^{II} atom.

The whole ligand is nearly planar, except for the C9–C14 phenyl ring, which is twisted by an angle of 6.9 (1)° from the pyridyl ring. This planarity is mainly due to the double-bond character of C6—N2 and C8—N3 of the thiosemicarbazone moiety joining the phenyl and pyridyl rings. The phenyl ring is hydrogen bonded to the thiosemicarbazone *via* an intermolecular C14—H14···N3 hydrogen bond, forming a six-membered N3—C8—N4—C9—C14—H14 ring (Fig. 1).

In the crystal, the molecules are linked by intermolecular N4—H4*A*···S1′, C7—H7*C*···N3′ and C11—H11···N3′ interactions (see Table 2 for details and symmetry codes) into a three-dimensional network (Fig. 2).

Experimental

The 2-acetylpyridine *N*(4)-phenylthiosemicarbazone ligand was prepared according to the procedure of Klayman *et al.* (1979). A hot ethanol solution of $MnCl_2{\cdot}4H_2O$ (0.198 g, 1 mmol) was added to a hot ethanol solution of 2-acetylpyridine *N*(4)-phenylthiosemicarbazone (2 mmol). The resulting mixture was warmed gently for 1 h with stirring. The light-yellow compound which separated was collected, washed with ethanol and ether, and finally dried over P_4O_{10} *in vacuo*. Brown single crystals suitable for X-ray analysis were obtained from a dimethylformamide solution after three weeks.

Crystal data

$[Mn(C_{14}H_{13}N_4S)_2]$
M_r = 593.63
Monoclinic, *C*2/*c*
a = 13.5897 (1) Å
b = 18.7968 (1) Å
c = 10.9688 (1) Å
β = 96.427 (1)°
V = 2784.29 (4) Å^3
Z = 4
D_x = 1.416 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 5869 reflections
θ = 2.5–28.3°
μ = 0.66 mm^{-1}
T = 183 (2) K
Block, brown
0.24 × 0.20 × 0.16 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.858, T_{max} = 0.902
8419 measured reflections
3381 independent reflections
2456 reflections with $I > 2\sigma(I)$
R_{int} = 0.090
θ_{max} = 28.3°
h = −10 → 17
k = −24 → 24
l = −14 → 14

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.145
S = 0.98
3381 reflections
182 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0641P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.75 e Å^{-3}
$\Delta\rho_{min}$ = −1.34 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—N2	2.258 (2)	Mn1—S1	2.5137 (8)
Mn1—N1	2.264 (2)		
N2^{i}—Mn1—N1	101.51 (8)	N2^{i}—Mn1—S1	110.27 (6)
N2—Mn1—N1	71.70 (8)	N2—Mn1—S1	76.09 (6)

Symmetry code: (i) $-x, y, \frac{3}{2}-z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4*A*···S1^{i}	0.84 (3)	2.74 (3)	3.494 (3)	151 (3)
C7—H7*C*···N3^{ii}	0.96	2.51	3.472 (4)	176
C11—H11···N3^{iii}	0.93	2.57	3.365 (4)	143
C14—H14···N3	0.93	2.34	2.927 (4)	121

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

H atoms were fixed geometrically and treated as riding on their parent C atoms, with C—H distances in the range 0.93–0.96 Å and $U_{iso}(H) = 1.2U_{eq}(C)$, except for atom H4*A*, which was located from a difference map and refined isotropically.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL, PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1569). Services for accessing these data are described at the back of the journal.

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