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**Key indicators**Single-crystal X-ray study  
 $T = 298$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.027  
 $wR$  factor = 0.072  
Data-to-parameter ratio = 14.9For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.***cis*-Aquadichloro(1,10-phenanthroline- $\kappa^2N,N'$ )-  
(thiourea- $\kappa S$ )manganese(II) thiourea solvate**

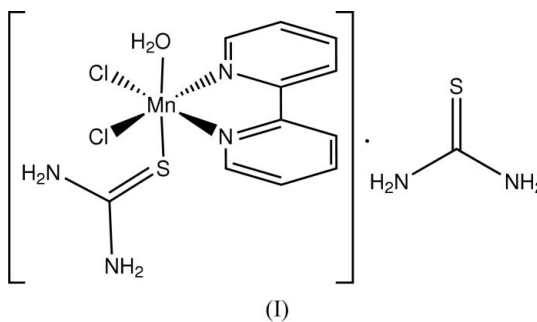
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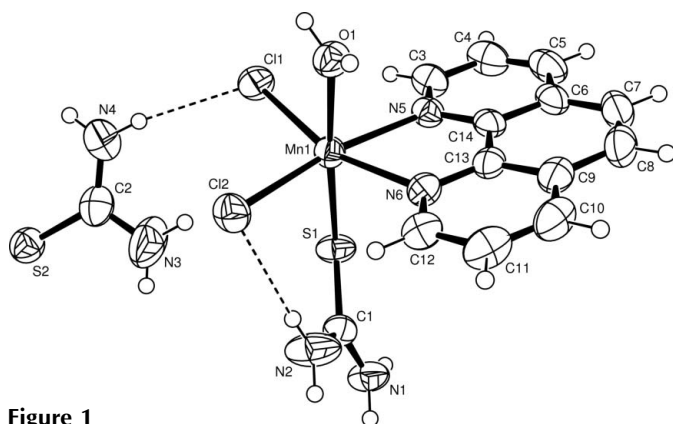
The title compound,  $[\text{MnCl}_2(\text{C}_{12}\text{H}_8\text{N}_2)\{(\text{NH}_2)_2\text{CS}\}(\text{H}_2\text{O})] \cdot (\text{NH}_2)_2\text{CS}$ , displays a distorted octahedral coordination geometry. The coordinated thiourea and water ligands are in *trans* positions, while the two  $\text{Cl}^-$  ions are in *cis* positions. In the crystal structure, a three-dimensional supramolecular structure involving hydrogen bonding and aromatic stacking is observed.

**Comment**

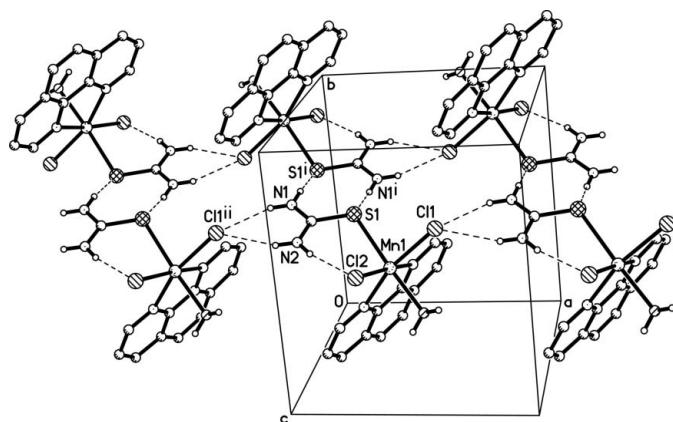
Some complexes of manganese have served as mimics for manganese catalases and extradiol-cleaving catechol dioxygenase (Triller *et al.*, 2002, 2003). The structural study of transition metal complexes containing sulfur coordination is helpful for catalysis (Stiefel, 1996) and medicinal chemistry (Jurisson *et al.*, 1993). As a ligand containing an S atom, thiourea (tu) is an interesting reagent for versatile coordination modes. However, to the best of our knowledge, no crystal structure of a manganese complex of thiourea has been reported. During our preparation of the  $\text{Mn}^{\text{II}}$  complex chelated by 4,5-diazafluoren-9-one (dafone) (Wu & Xu, 2004), we found that the  $\text{Mn}^{\text{II}}$  atom prefers to be chelated by poor dafone ligands (Menon & Rajasekharan, 1997) rather than being coordinated by thiourea, which is in contrast to other first-row transition metal ions such as  $\text{Cu}^{\text{I}}$ , *etc.* (Wu *et al.*, 2002). Recently, the title compound, (I), was obtained using 1,10-phenanthroline (phen) as the ligand instead of dafone and the crystal structure is presented here.



The crystal structure of (I) is built of  $\text{Mn}^{\text{II}}$  complexes and uncoordinated thiourea molecules. The complex molecule has a distorted octahedral coordination geometry (Fig. 1). The coordinated water (O1) and thiourea (S1) each occupy an axial position. In the equatorial plane, the  $\text{Mn}^{\text{II}}$  ion is coordinated by the chelating phen ligand and two  $\text{Cl}^-$  anions in *cis* positions; the maximum deviation from the mean plane is 0.1337 (9) Å (N5). The title compound is structurally similar to the  $\text{Co}^{\text{II}}$  analog (Suescun *et al.*, 1999). The coordination



**Figure 1**  
The asymmetric unit of (I). Displacement ellipsoids are drawn at the 50% probability level. The dashed lines indicate hydrogen bonds.



**Figure 2**  
A one-dimensional hydrogen-bonded chain of complex molecules. The dashed lines indicate hydrogen bonds. [Symmetry codes: (i)  $-x, 1 - y, -z$ ; (ii)  $x - 1, y, z$ .]

bonds are a little longer than the corresponding ones of the latter (Table 1), which is consistent with the larger ionic radius of  $\text{Mn}^{\text{II}}$ . The bite angle of phen is  $73.23(7)^\circ$ , which is smaller than in the  $\text{Co}^{\text{II}}$  complex [ $77.33(9)^\circ$ ].

The thiourea ligands are hydrogen bonded to neighboring complex molecules, which thus form chains along the  $a$ -axis direction (Fig. 2 and Table 2). The uncoordinated thiourea molecules are involved in hydrogen bonds as acceptor for water molecules and as donor to Cl atoms (Fig. 3). Consequently, through thiourea molecules (coordinated and uncoordinated), a three-dimensional hydrogen-bonding structure is formed in the crystal structure. Furthermore, aromatic stacking along the  $a$ -axis direction occurs between adjacent hydrogen-bonding chains.  $\pi$ - $\pi$  Stacking of phen ligands occurs between the phen ring at  $(x, y, z)$  and those related by symmetry operations (iv)  $(-x, -y, -z)$  and (v)  $(1 - x, -y, -z)$  (Fig. 3). The nearest separation is  $3.350(3) \text{ \AA}$  to  $\text{Cl}10^{\text{v}}$ .

## Experimental

Phen (0.05 g, 0.28 mmol) and thiourea (0.038 g, 0.5 mmol) were added to a 15 ml ethanol (90%) and 5 ml acetonitrile solution containing  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (0.05 g, 0.25 mmol). The solution was

refluxed for 40 min and filtered, and the filtrate was kept at room temperature. Yellow crystals of a suitable size were obtained after 4 d. Analysis calculated for  $\text{C}_{14}\text{H}_{18}\text{Cl}_2\text{MnN}_6\text{O}_2\text{S}$ : C 35.30, H 3.81, N 17.64%; found: C 35.03, H 3.77, N 17.95%.

## Crystal data

$[\text{MnCl}_2(\text{C}_{12}\text{H}_8\text{N}_2)(\text{CH}_4\text{N}_2\text{S}) \cdot (\text{H}_2\text{O})] \cdot \text{CH}_4\text{N}_2\text{S}$   
 $M_r = 476.30$   
 Triclinic,  $P\bar{1}$   
 $a = 8.8590(18) \text{ \AA}$   
 $b = 9.811(2) \text{ \AA}$   
 $c = 11.706(2) \text{ \AA}$   
 $\alpha = 86.46(3)^\circ$   
 $\beta = 87.04(3)^\circ$

$\gamma = 89.89(3)^\circ$   
 $V = 1014.1(3) \text{ \AA}^3$   
 $Z = 2$   
 $D_x = 1.560 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 $\mu = 1.14 \text{ mm}^{-1}$   
 $T = 298(2) \text{ K}$   
 Prism, yellow  
 $0.25 \times 0.15 \times 0.10 \text{ mm}$

## Data collection

Bruker APEX area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2002)  
 $T_{\text{min}} = 0.764, T_{\text{max}} = 0.895$

5498 measured reflections  
 3619 independent reflections  
 2984 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.011$   
 $\theta_{\text{max}} = 25.2^\circ$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.027$   
 $wR(F^2) = 0.072$   
 $S = 1.03$   
 3619 reflections  
 243 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0341P)^2 + 0.3271P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters ( $\text{\AA}, ^\circ$ ).

Mn1—S1	2.6758 (11)	S1—C1	1.708 (2)
Mn1—Cl1	2.4884 (10)	S2—C2	1.694 (3)
Mn1—Cl2	2.4783 (9)	N1—C1	1.319 (3)
Mn1—O1	2.2247 (19)	N2—C1	1.309 (3)
Mn1—N5	2.2971 (18)	N3—C2	1.312 (4)
Mn1—N6	2.2540 (19)	N4—C2	1.319 (3)
Cl1—Mn1—Cl2	98.26 (4)	O1—Mn1—S1	174.64 (5)
N5—Mn1—N6	73.23 (7)	Cl1—S1—Mn1	112.52 (8)
Mn1—S1—Cl1—N1	-153.46 (17)	Mn1—S1—Cl1—N2	27.8 (2)

**Table 2**

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1A $\cdots$ S1 <sup>i</sup>	0.86	2.57	3.383 (2)	157
N1—H1B $\cdots$ Cl1 <sup>ii</sup>	0.86	2.41	3.239 (2)	162
N2—H2A $\cdots$ Cl1 <sup>iii</sup>	0.86	2.75	3.504 (2)	147
N2—H2B $\cdots$ Cl2	0.86	2.45	3.295 (3)	168
O1—H1C $\cdots$ S2 <sup>iii</sup>	0.87 (4)	2.40 (4)	3.260 (2)	173 (3)
O1—H1D $\cdots$ S2 <sup>iv</sup>	0.84 (3)	2.36 (3)	3.177 (2)	164 (3)
N4—H4A $\cdots$ Cl1	0.86	2.45	3.290 (3)	167
N4—H4B $\cdots$ Cl2 <sup>v</sup>	0.86	2.77	3.513 (3)	146

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

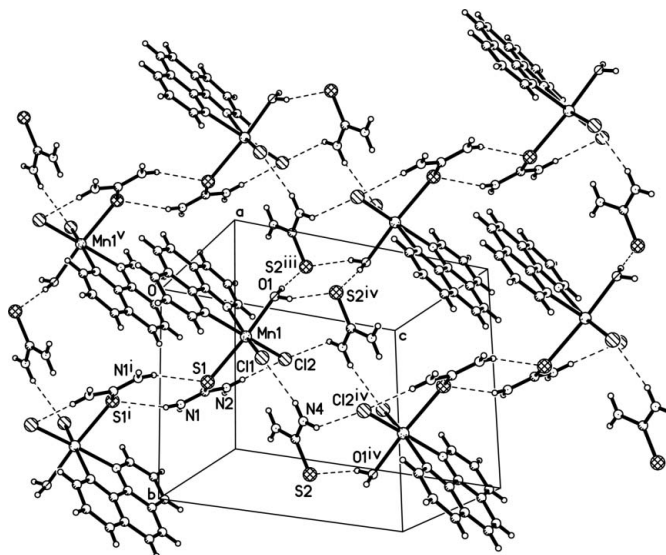
The H atoms of water molecules were located in a difference Fourier map and refined freely; the O–H distances are 0.87 (4) and 0.84 (3) Å. H atoms of aromatic rings and terminal amine groups were placed in calculated positions, with C–H = 0.93 Å and N–H = 0.86 Å, and were included in the final cycles of refinement in a riding model, with  $U_{\text{iso}}(\text{H})$  values equal to  $1.2U_{\text{eq}}$  of the carrier atoms.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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**Figure 3**

A packing diagram. Thiourea molecules play a key role in the three-dimensional hydrogen-bonding structure. A  $\pi$ – $\pi$  stacking interaction along the  $a$  axis is observed between phen and phen<sup>v</sup>. [Symmetry codes: (i)  $-x, 1-y, -z$ ; (iii)  $x, y-1, z$ ; (iv)  $1-x, 1-y, 1-z$ ; (v)  $-x, -y, -z$ .]

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