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cis-(2,2′-Bipyridyl)dichloromanganese(II)–thiourea (1/1)

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.010 Å
R factor = 0.086
wR factor = 0.183
Data-to-parameter ratio = 14.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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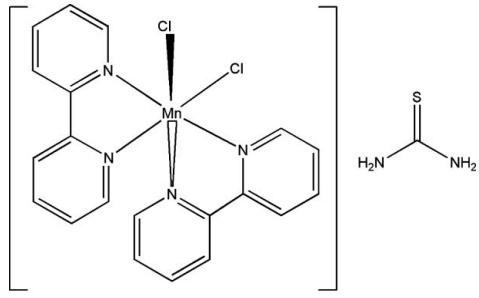
In the title compound, $[MnCl_2(C_{10}H_8N_2)_2]\cdot SC(NH_2)_2$, the Mn^{II} atom is coordinated by four N atoms from two 2,2′-bipyridyl ligands and two Cl^- anions, resulting in a distorted *cis*-$MnCl_2N_4$ octahedral geometry. The complexes and thiourea molecules are connected by N—H···Cl and N—H···S hydrogen bonds, leading to one-dimensional tapes which are further organized into a three-dimensional structure through π–π, C—H···π and C—H···Cl interactions.

Comment

A one-pot reaction between $MnCl_2$, 2,2′-bipyridine (2,2′-bpy) and thiourea in aqueous/methanolic solution resulted in the title complex, (I). Selected geometric data are listed in Table 1 and the molecular conformation is illustrated in Fig. 1.



(I)

The asymmetric unit of compound (I) consists of a neutral complex accompanied by one thiourea molecule. In the complex, the Mn atom is coordinated by two Cl^- ions and four N atoms (from two bidentate 2,2′-bipyridyl ligands), forming a *cis*-$MnCl_2N_4$ octahedral geometry, similar to that seen in the related compounds $[Mn(2,2'\text{-bpy})_2Cl_2]$ (Lumme & Lindell, 1988), $[Mn(2,2'\text{-bpy})_2Cl_2]\cdot C_2H_5OH\cdot 2H_2O$ (McCann *et al.*, 1998) and $[Mn(2,2'\text{-bpy})_2Cl_2]\cdot C_{10}H_8N_2\cdot H_2O$ (Li *et al.*, 2002).

The supramolecular interactions in (I) are listed in Table 2. Compared with the complexes noted above, the weak interactions and crystal packing are totally changed because of the presence of the thiourea molecule in (I). In particular, the complexes and thiourea molecules in (I) are connected through various hydrogen-bonded rings built from N—H···Cl and N—H···S hydrogen bonds. There are two eight-membered rings, both with graph-set notation $R_2^2(8)$ (Bernstein *et al.*, 1995). One ring (Cl1/Mn1/Cl2/N5/C21/N6) connects complex and thiourea molecules and the other [S1/C21/N6/S1^i/C21^i/N6^i; symmetry code: (i) $2-x, 1-y, 2-z$] connects inversion-related thiourea molecules. This pairing of thiourea molecules may be termed 'self recognition' or 'self

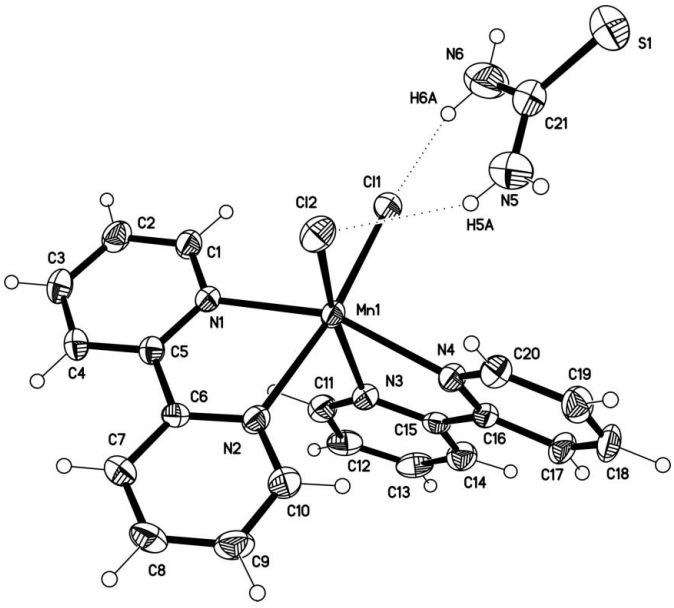


Figure 1
The asymmetric unit of (I), with displacement ellipsoids drawn at the 30% probability level (arbitrary spheres for the H atoms). Dotted lines indicate hydrogen bonds.

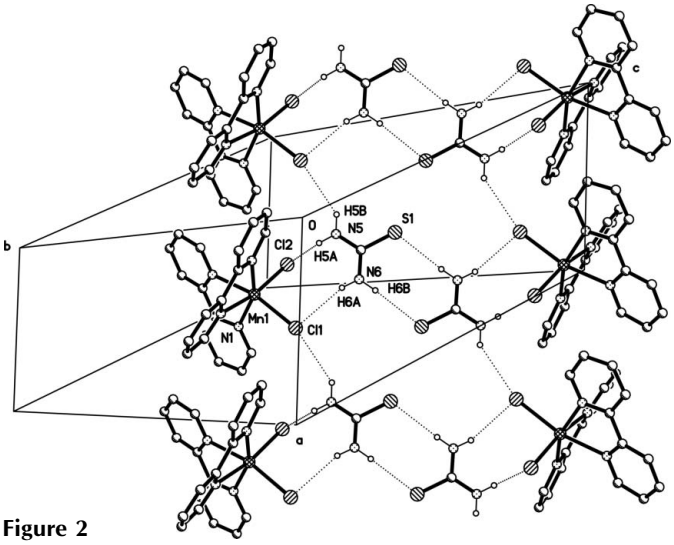


Figure 2
Detail of the crystal structure of (I), showing the one-dimensional tape built from N—H···Cl and N—H···S interactions (dotted lines). H atoms not involved in hydrogen bonding have been omitted.

assembly'. Finally, a sixteen-membered $R_6^4(16)$ ring [Cl1/N6/S1^{i}/C21^{i}/N5^{i}/Cl1^{ii}/N6^{ii}/S1^{iii}/C21^{iii}/N5^{iii}; symmetry codes: (ii) $3-x, 1-y, 2-z$; (iii) $1+x, y, z$] helps to establish one-dimensional tapes along the *a* axis (Fig. 2).

These tapes are further linked into a three-dimensional structure through π–π stacking interactions between inversion-related six-membered rings (N4/C16/C17/C18/C19/C20), with a centroid–centroid^{iv} [symmetry code: (iv) $1-x, 1-y, 1-z$] distance of 3.761 (4) Å and a perpendicular separation of 3.415 Å, and a C—H···π interaction with a C12···Cg^{v} [*Cg* is the centroid of the ring N1/C1–C5; symmetry code: (v) $x, \frac{3}{2}-y, z-\frac{1}{2}$] distance of 3.718 Å, as well as a C18—H18···Cl1 hydrogen bond (Fig. 3).

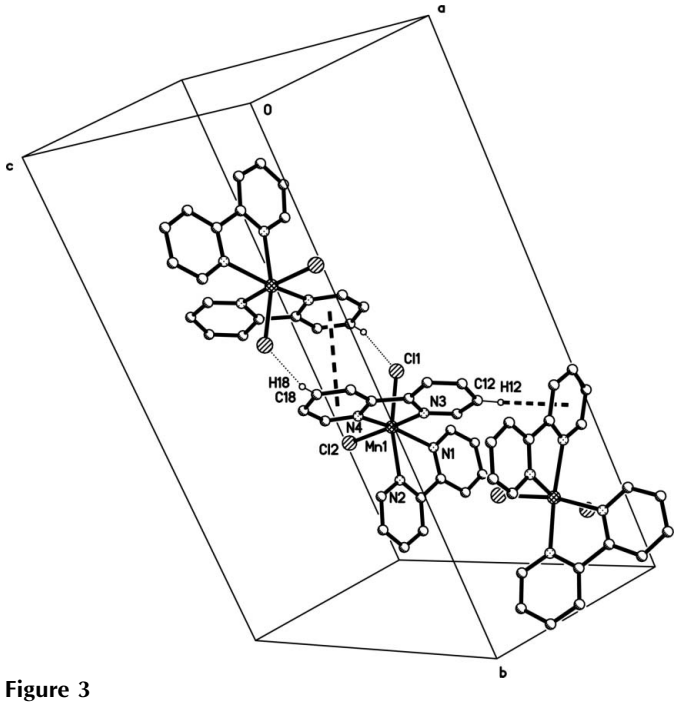


Figure 3
Detail of the crystal structure of (I), showing the C—H···π interactions and π–π stacking interactions (dashed lines), and the C—H···Cl—Mn hydrogen bonding (dotted lines). H atoms not involved in the various interactions have been omitted for clarity.

Experimental

$MnCl_2$ (0.252 g, 2 mmol) was dissolved in water (30 ml) to give a clear solution. To this solution, 2,2′-bipyridine (0.624 g, 4 mmol) dissolved in methanol (20 ml) was added. A light-yellow solution resulted. To this solution, thiourea (0.076 g, 1 mmol) dissolved in the minimum volume of water was added. The resulting light-yellow solution was heated at 323 K for 1 h with continuous stirring and the solution was then allowed to cool. It was then filtered and kept for crystallization. Light-yellow rectangular-block crystals of (I) separated after several days as the mother liquor slowly evaporated at room temperature. The crystals were separated by filtration, washed with cold water and air-dried (0.36 g, yield 70%). Analysis, calculated for $C_{21}H_{20}N_6Cl_2SMn$: C 49.03, H 3.89, N 16.34%; found: C 49.31, H 4.1, N 16.2%.

Crystal data

$[MnCl_2(C_{10}H_8N_2)_2]\cdot CH_4N_2S$
$M_r = 514.33$
Monoclinic, $P2_1/c$
$a = 7.3555\ (13)$ Å
$b = 23.433\ (4)$ Å
$c = 14.5730\ (18)$ Å
$\beta = 115.459\ (6)^\circ$
$V = 2267.9\ (6)$ Å^3
$Z = 4$
$D_x = 1.506$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.93$ mm^{-1}
$T = 298\ (2)$ K
Block, yellow
0.40 × 0.30 × 0.20 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
$T_{min} = 0.707$, $T_{max} = 0.836$
10930 measured reflections
3987 independent reflections
3532 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 25.0^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 6.0756P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.086$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.183$	$\Delta\rho_{max} = 0.61$ e Å^{-3}
$S = 1.31$	$\Delta\rho_{min} = -0.52$ e Å^{-3}
3987 reflections	
280 parameters	
H-atom parameters constrained	

Table 1
Selected bond lengths (Å).

Mn1—N1	2.275 (5)	Mn1—N3	2.306 (5)
Mn1—N4	2.285 (5)	Mn1—Cl2	2.450 (2)
Mn1—N2	2.289 (5)	Mn1—Cl1	2.484 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N6—H6B···S1^{i}	0.86	2.67	3.490 (8)	161
N6—H6A···Cl1	0.86	2.74	3.520 (8)	151
N5—H5B···Cl1^{ii}	0.86	2.86	3.588 (8)	144
N5—H5A···Cl2	0.86	2.44	3.197 (8)	147
C18—H18···Cl1^{iii}	0.93	2.74	3.649 (8)	164

Symmetry codes: (i) $-x+2, -y+1, -z+2$; (ii) $x-1, y, z$; (iii) $-x+1, -y+1, -z+1$.

H atoms were placed in geometrically idealized positions, with Csp^2—H = 0.93 Å and Nsp^2—H = 0.86 Å, and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C,N).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

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