

***trans*-Bis(isothiocyanato- κ N)-bis(methanol- κ O)bis[2,4,6-tri(4-pyridyl)-1,3,5-triazine- κ N²]manganese(II)**

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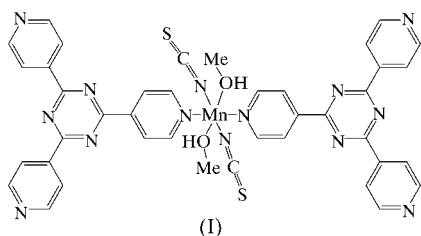
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The title compound, $[\text{Mn}(\text{NCS})_2(\text{C}_{18}\text{H}_{12}\text{N}_6)_2(\text{CH}_4\text{O})_2]$, contains a centrosymmetric octahedral Mn^{II} centre and three pairs of *trans*-coordinating ligands. It is the first example of a mononuclear metal complex with the 2,4,6-tri(4-pyridyl)-1,3,5-triazine (tpt) ligand. Intermolecular π - π stacking of the planar tpt ligands, as well as hydrogen bonds between pyridyl N and methanol H atoms, results in the formation of a three-dimensional network.

Comment

The simple trigonal building block 2,4,6-tri(4-pyridyl)-1,3,5-triazine (tpt) has been utilized as a bridging unit for coordination polymers with diverse structures (Batten *et al.*, 1995*a,b*; Abrahams, Batten, Hamit *et al.*, 1996; Abrahams, Batten,



Grannas *et al.*, 1996; Abrahams *et al.*, 1999), and as a template in the synthesis of porphyrin (Anderson *et al.*, 1995) or phthalocyanine (Hanak *et al.*, 1999) oligomers. In the course of our efforts to explore new supramolecular architectures using tpt and NCS^- ligands, the title compound, (I), was unexpectedly isolated, and it has been characterized by single-crystal X-ray analysis. To our knowledge, this is the first example of a mononuclear tpt metal complex.

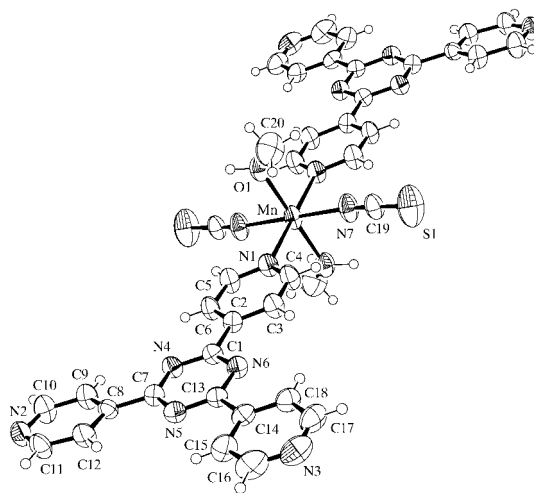
The molecular unit of (I) comprises two tpt ligands, two NCS^- anions and two methanol ligands. As shown in Fig. 1, the molecule possesses crystallographic inversion symmetry on the metal ion, and thus each ligand pair is coordinated with a *trans* geometry, resulting in a distorted octahedral environment around Mn^{II} .

It should be noted that tpt uses only one of three possible N atoms in coordinating to the metal ion. The $\text{Mn}-\text{N}_{\text{tpt}}$ bond distances are longer than the $\text{Mn}-\text{O}$ and $\text{Mn}-\text{N}_{\text{NCS}}$ distances. The $\text{Mn}-\text{N}_{\text{tpt}}$ bond distance is 2.355 (3) Å, which is consistent with the value of 2.360 (4) Å found in $[\text{Mn}L_2(\text{H}_2\text{O})_2(\text{SCN})_2]$ [L is 2,5-bis(4-pyridyl)-1,3,4-oxadiazole; Fang *et al.*, 2002], but somewhat longer than the value of 2.31 (1) Å found in the linear polymeric complex $[\text{Mn}(\text{bpe})(\text{NCS})_2(\text{CH}_3\text{OH})_2]_n$ [bpe is *trans*-1,2-bis(4-pyridyl)ethene; De Munno *et al.*, 1999].

The $\text{Mn}-\text{N}_{\text{NCS}}$ bond distance is 2.139 (3) Å, in good agreement with the sum of the Shannon (1976) ionic radii (2.13 Å) and the $\text{Mn}^{\text{II}}-\text{N}_{\text{NCS}}$ distance of 2.141 (7) Å observed in $[\text{Mn}(\text{tbr})_3(\text{NCS})(\text{H}_2\text{O})]_n$ (tbr is 4,4'-bis-1,2,4-triazole; Zilverentant *et al.*, 1998). However, this $\text{Mn}-\text{N}_{\text{NCS}}$ distance is slightly shorter than that found in $[\text{Mn}(\mu\text{-}4,4'\text{-bipyridine})(4,4'\text{-bipyridine})(\text{NCS})_2(\text{H}_2\text{O})_2]_n$ [2.188 (8) Å; Li *et al.*, 1995] and considerably shorter than that found in $[\text{Mn}(\text{bpe})(\text{NCS})_2(\text{CH}_3\text{OH})_2]_n$ [2.24 (2) Å; De Munno *et al.*, 1999]. As an explanation of such bond lengthening in this last complex, it was suggested that the thiocyanate groups are involved in hydrogen-bond formation. The $\text{Mn}-\text{O1}$ distance in (I) [2.213 (3) Å] is in the usual range. The thiocyanate ligand has the expected linear geometry, with an $\text{N}-\text{C}-\text{S}$ angle of 178.5 (3)°.

The mean atomic displacement from the least-squares plane of the tpt ligand is 0.079 Å. However, the value for the plane excluding the N2-pyridyl ring is only 0.018 Å. The N2-pyridyl ring forms a dihedral angle of 7.8 (2)° with the central C_3N_3 ring, while the corresponding values for the N1- and N3-pyridyl rings are 1.9 (2) and 0.9 (2)°, respectively. The distortion of the N2-pyridyl ring is caused by the hydrogen bond between N2 and the methanol H atom (Table 2), and this hydrogen bond forms a one-dimensional linear chain structure along the [011] direction, as shown in Fig. 2.

The shortest intrachain separation of Mn atoms is 14.413 (4) Å. In addition, the molecules are stacked with the

**Figure 1**

A view of the molecule of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

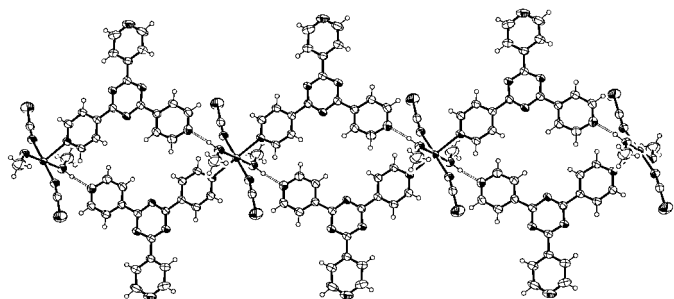


Figure 2
The one-dimensional linear chain structure of (I), formed by hydrogen bonding.

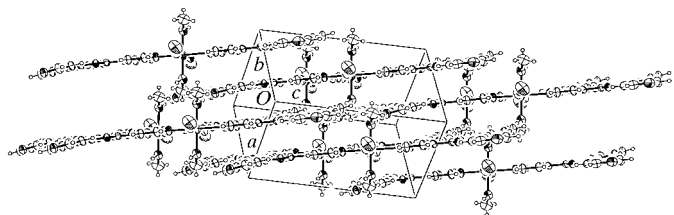


Figure 3
A two-dimensional molecular packing diagram for (I).

closest approach between the aromatic rings being *ca* 3.29 Å, leading to the formation of a two-dimensional structure, as depicted in Fig. 3. These two-dimensional layers are stacked further by π - π interactions to form a three-dimensional network.

Experimental

A solution of tpt (0.2 mol) in dichloromethane (20 ml) was added to a solution of an excess of potassium thiocyanate in methanol (10 ml). The mixture was stirred for 10 min and treated with a solution of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol) in methanol (10 ml). After stirring for 2 h at ambient temperature, the resulting solution was set aside to crystallize, producing analytically pure (I). A crystal of (I) suitable for X-ray diffraction analysis was selected directly from the analytical sample.

Crystal data

$[\text{Mn}(\text{NCS})_2(\text{C}_{18}\text{H}_{12}\text{N}_6)_2(\text{CH}_4\text{O})_2]$	$Z = 1$
$M_r = 859.86$	$D_x = 1.406 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.871 (2) \text{ \AA}$	Cell parameters from 25 reflections
$b = 8.875 (2) \text{ \AA}$	$\theta = 23\text{--}29^\circ$
$c = 14.161 (4) \text{ \AA}$	$\mu = 0.48 \text{ mm}^{-1}$
$\alpha = 106.54 (2)^\circ$	$T = 293 (2) \text{ K}$
$\beta = 100.60 (2)^\circ$	Needle, yellow
$\gamma = 100.93 (3)^\circ$	$0.32 \times 0.17 \times 0.15 \text{ mm}$
$V = 1015.3 (4) \text{ \AA}^3$	

Table 1

Selected geometric parameters (Å, °).

Mn—N7	2.139 (3)	S1—C19	1.609 (4)
Mn—O1	2.213 (3)	O1—C20	1.425 (5)
Mn—N1	2.355 (3)	N7—C19	1.155 (4)
N7—Mn—O1	91.03 (12)	C20—O1—Mn	128.8 (3)
N7—Mn—N1	89.57 (11)	C19—N7—Mn	164.5 (3)
O1—Mn—N1	86.55 (10)	N7—C19—S1	178.5 (3)

Data collection

Enraf–Nonius CAD-4
diffractometer
 $\theta/2\theta$ scans
3732 measured reflections
3571 independent reflections
2796 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.015$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.132$
 $S = 1.01$
3571 reflections
268 parameters
H-atom parameters constrained

$\theta_{\text{max}} = 25^\circ$
 $h = -10 \rightarrow 10$
 $k = -10 \rightarrow 10$
 $l = 0 \rightarrow 16$
3 standard reflections
frequency: 120 min
intensity decay: none

$w = 1/[\sigma^2(F_o^2) + (0.0374P)^2 + 1.8244P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.028$
 $\Delta\rho_{\text{max}} = 0.33 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.40 \text{ e \AA}^{-3}$

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O1—HO1 \cdots N2 ⁱ	0.96	1.77	2.721 (4)	173

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

Data collection: *MACH3* (Enraf–Nonius, 1996); cell refinement: *CELDIM* (Enraf–Nonius, 1996); data reduction: *XCAD4* (Harms & Wocadlo, 1995); structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1080). Services for accessing these data are described at the back of the journal.

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