

## Poly[[bis(dimethyl sulfoxide- $\kappa$ O)tris-(thiocyanato- $\kappa$ N)manganese(II)]- $\mu$ -thiocyanato- $\kappa^2$ N:S-mercury(II)]

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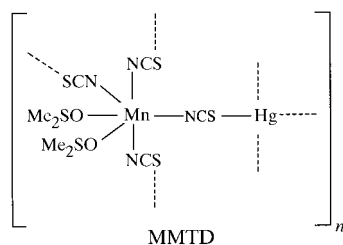
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In the title complex,  $[\text{MnHg}(\text{SCN})_4(\text{C}_2\text{H}_6\text{SO})_2]_n$ , each Hg atom is tetrahedrally coordinated to four S atoms of the SCN ions, while each Mn atom is octahedrally coordinated to four N atoms of the SCN ions and two O atoms of the dimethyl sulfoxide molecules which occupy the *trans* positions. Each pair of Hg and Mn atoms is bridged by one SCN ion. Two Mn atoms, two Hg atoms and four SCN ions make a 16-membered ring which organises into a two-dimensional network. The dimethyl sulfoxide ligands are extended perpendicular to the plane on both sides.

### Comment

There is considerable interest in the synthesis of new materials with excellent second-order optical non-linearities. During the last few years, the field of organometallic and coordination complexes has seen much activity with the search for useful non-linear optical (NLO) materials, because such complexes have the potential to combine the high optical non-linearity and chemical flexibility of organics with the physical ruggedness of inorganics (Long, 1995). Many new metal-organic NLO crystals have been successfully found on the basis of



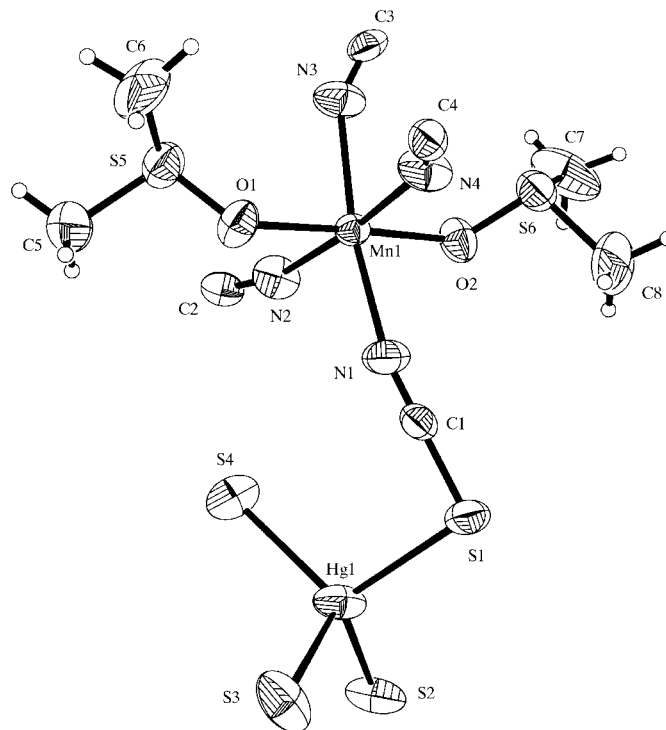
molecular engineering and the double-ligand model (Xu *et al.*, 1987, 1994, 1999; Tao *et al.*, 1987; Zhang *et al.*, 1989; Yuan *et al.*, 1990, 1997; Yu *et al.*, 1991; Hou *et al.*, 1993; Wang, 1996; Tian *et al.*, 1997). The compound manganese mercury tetrathiocyanate,  $\text{MnHg}(\text{SCN})_4$  (MMTC), was reported by Yan *et al.* (1999), and the crystal shows a 532 nm second harmonic

intensity 18 times that of the crystal urea. The title compound, MMTD, is the dimethyl sulfoxide (DMSO) adduct of MMTC and is a new NLO crystal. It exhibits a strong NLO effect and is easy to grow into large crystals. Its crystal structure is presented here.

The concept of hard and soft acids and bases tells us that hard cations such as  $\text{Mn}^{2+}$  and  $\text{Co}^{2+}$  show a pronounced affinity for coordination with harder ligands, while soft cations such as  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  prefer coordination with softer ligands (Pearson, 1963, 1966; Balarew & Duhlew, 1984; Yamaguchi *et al.*, 1985; Ozutsumi *et al.*, 1989). In the structure of MMTD, the hard  $\text{Mn}^{2+}$  ion is coordinated with the harder N (SCN) and O (DMSO) ligands, while the soft  $\text{Hg}^{2+}$  ion is coordinated with the softer S (SCN) ligands.

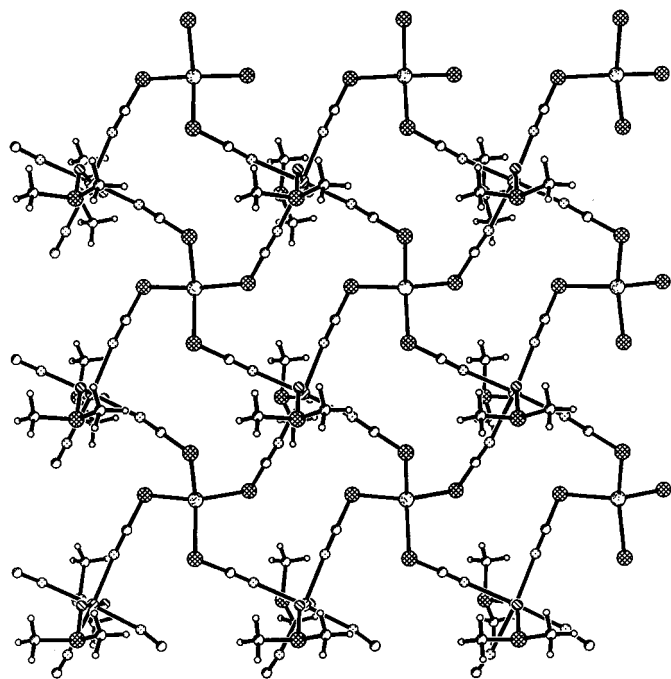
The  $\text{Hg}^{2+}$  ion is coordinated with four SCN S atoms and is in a tetrahedral geometry. The  $\text{Mn}^{2+}$  ion is six-coordinate and is in an octahedral geometry; both of the O atoms of the DMSO molecules are coordinated axially, while four SCN N atoms are coordinated equatorially. The average Hg—S length is 2.545 Å and the average bond angle around the Hg atom is 109.48° [range 105.97 (12)–113.84 (11)°], which is slightly different from typical tetrahedral angles.

The average Mn—N and Mn—O bond lengths are 2.222 Å and 2.156 Å, respectively. These values are about the same as the lengths in common octahedral manganese(II) complexes. The average bond angles for N—Mn—O and N—Mn—N (between vicinal N atoms) are 90.0 and 90.2°, respectively. The O—Mn—O angle is little distorted from 180° at 177.8 (3)°.



**Figure 1**  
The molecular structure of MMTD showing 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

Overall, the tetrahedral geometry of the Hg core and the octahedral geometry of the Mn core are both slightly deformed from the ideal forms. The most striking features are the  $-\text{S}=\text{C}=\text{N}-$  bridges which connect Mn and Hg, forming an infinite two-dimensional network. The macroscopic non-linear susceptibility may be related to the microscopic hyperpolarizabilities of the dipolar SCN ions, just as in MMTC, and to the distorted  $\text{HgS}_4$  tetrahedra and  $\text{MnN}_4\text{O}_2$  octahedra (Zyss, 1991). What is more, the average Mn–N–C bond angle is  $156.1^\circ$ , which is significantly different from  $180^\circ$ ; such large distortions of these angles are probably due to steric hindrance to the formation of planar complex networks in the crystal. Also, the DMSO ligands coordinated to  $\text{Mn}^{2+}$  are extended approximately perpendicular to the complex layer. The interaction of the DMSO adduct base renders this new crystal structure much more distorted than that of the original crystal, MMTC. The novel infinite two-dimensional network confers larger polarization, which in turn, we believe, induces greater macroscopic non-linearity than MMTC. The second harmonic generation (SHG) of the crystals was studied by the power SHG method (Kurtz & Perry, 1968). It was found that MMTD crystals are superior to those of MMTC.



**Figure 2**  
Packing diagram for MMTD showing the two-dimensional network.

## Experimental

A crystalline powder of MMTC was added to a mixed solvent of DMSO and water. This mixture was heated and stirred until the MMTC had dissolved. The colourless solution was left at room temperature until crystals of MMTD were formed.

## Crystal data

$[\text{MnHg}(\text{SCN})_4(\text{C}_2\text{H}_6\text{SO})_2]$   
 $M_r = 644.11$   
 Orthorhombic,  $P2_12_12_1$   
 $a = 8.4937$  (6) Å  
 $b = 8.5226$  (4) Å  
 $c = 27.884$  (4) Å  
 $V = 2018.5$  (3) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 2.120$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 35 reflections  
 $\theta = 5.73\text{--}12.96^\circ$   
 $\mu = 8.849$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Orthorhombic, colourless  
 $0.25 \times 0.22 \times 0.20$  mm

## Data collection

Bruker P4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  $\psi$  scan  
 (XSCANS; Siemens, 1996)  
 $T_{\min} = 0.119$ ,  $T_{\max} = 0.165$   
 3460 measured reflections  
 2659 independent reflections (plus 572 Friedel-related reflections)  
 2310 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.035$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -1 \rightarrow 11$   
 $k = -1 \rightarrow 11$   
 $l = -1 \rightarrow 36$   
 3 standard reflections every 97 reflections  
 intensity decay: none

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.043$   
 $wR(F^2) = 0.112$   
 $S = 1.027$   
 3231 reflections  
 200 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0513P)^2 + 2.4486P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.96$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -1.40$  e Å<sup>-3</sup>  
 Extinction correction: *SHELXTL* (Bruker, 1997)  
 Extinction coefficient: 0.0045 (2)  
 Absolute structure: Flack (1983)  
 Flack parameter = 0.004 (12)

**Table 1**  
Selected geometric parameters (Å, °).

Hg1–S4	2.538 (3)	Mn1–O1	2.158 (6)
Hg1–S2	2.539 (3)	Mn1–N2	2.196 (9)
Hg1–S3	2.549 (3)	Mn1–N1	2.199 (9)
Hg1–S1	2.552 (3)	Mn1–N4	2.244 (9)
Mn1–O2	2.153 (6)	Mn1–N3	2.248 (9)
S4–Hg1–S2	109.54 (12)	N1–Mn1–N4	88.2 (3)
S4–Hg1–S3	112.40 (11)	O2–Mn1–N3	86.4 (3)
S2–Hg1–S3	107.68 (13)	O1–Mn1–N3	95.3 (3)
S4–Hg1–S1	107.46 (11)	N2–Mn1–N3	91.2 (3)
S2–Hg1–S1	113.84 (11)	N4–Mn1–N3	86.9 (3)
S3–Hg1–S1	105.97 (12)	C1–N1–Mn1	163.3 (9)
O2–Mn1–O1	177.8 (3)	C2–N2–Mn1	161.1 (9)
O2–Mn1–N2	90.7 (3)	C3–N3–Mn1	149.6 (9)
O1–Mn1–N2	87.9 (3)	C4–N4–Mn1	150.5 (9)
O2–Mn1–N1	87.1 (3)	N1–C1–S1	179.4 (11)
O1–Mn1–N1	91.3 (3)	N2–C2–S3 <sup>i</sup>	178.7 (10)
N2–Mn1–N1	94.4 (3)	N3–C3–S2 <sup>ii</sup>	177.9 (10)
O2–Mn1–N4	95.1 (3)	N4–C4–S4 <sup>iii</sup>	178.6 (10)
O1–Mn1–N4	86.4 (3)		

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

The deepest hole in the final electron-density map is  $-1.40$  e Å<sup>-3</sup> at (0.4948, 0.7597, 0.0937), 0.87 Å from Hg1.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1349). Services for accessing these data are described at the back of the journal.

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