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Key indicators

Single-crystal X-ray study
 $T = 296$ K
Mean $\sigma(\text{C}-\text{C}) = 0.015$ Å
 R factor = 0.036
 wR factor = 0.072
Data-to-parameter ratio = 18.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Poly[[μ -aqua-tetra- μ -thiocyanato-manganese(II)-
mercury(II)] sulfolane solvate]

The title polymeric compound, $[\{\text{MnHg}(\text{SCN})_4(\text{H}_2\text{O})\} \cdot \text{C}_4\text{H}_8\text{O}_2\text{S}]_n$, consists of slightly distorted MnN_4O_2 octahedra and HgS_4 tetrahedra. Each Mn^{II} ion is bound to N atoms belonging to the thiocyanate (SCN) groups and to two O atoms of adjacent water ligands. The sulfolane molecule connects with the coordinated water molecule through hydrogen bonding. Each Hg^{II} atom is coordinated by four SCN S atoms. The two adjacent Mn^{II} atoms and two O atoms of bridging water molecules connect with one another and form a parallelogram. Each pair of Mn^{II} and Hg^{II} atoms is connected by an $-\text{SCN}-$ bridge, forming an infinite three-dimensional structure.

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Comment

Manganese mercury thiocyanate (MMTC) consists of distorted $\text{MnN}(\text{SCN})_4$ and $\text{HgS}(\text{SCN})_4$ tetrahedra (Yan *et al.*, 1999). Its three reported Lewis base (LB) [dimethyl sulfoxide (DMSO), glycol monomethyl ether (GME) and NMF (*N*-methylformamide), respectively] adducts contain distorted $\text{MnN}(\text{SCN})_4\text{O}(\text{LB})_2$ octahedra and $\text{HgS}(\text{SCN})_4$ tetrahedra (Wang, Yu, Xu, Lu & Yuan, 2000; Wang, Yu, Xu, Lu, Yuan, Liu & Lu, 2000; Wang, Yu, Xu, Lu, Yuan & Lu, 2000; Wang *et al.*, 2002). The urea adduct possesses a slightly distorted octahedral $\text{MnN}(\text{SCN})_3\text{O}(\text{urea})_3$ and tetrahedral $\text{HgS}(\text{SCN})_4$ (Wang *et al.*, 2002). The thiourea (TU) adduct (Yu *et al.*, 2001) consists of discrete $[\text{Hg}(\text{TU})_4]^{2+}$ and $[\text{Mn}(\text{SCN})_4]^{2-}$.

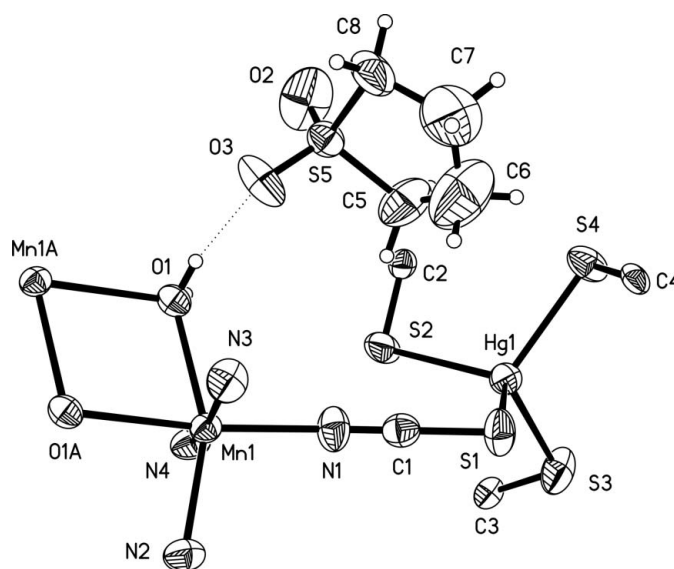
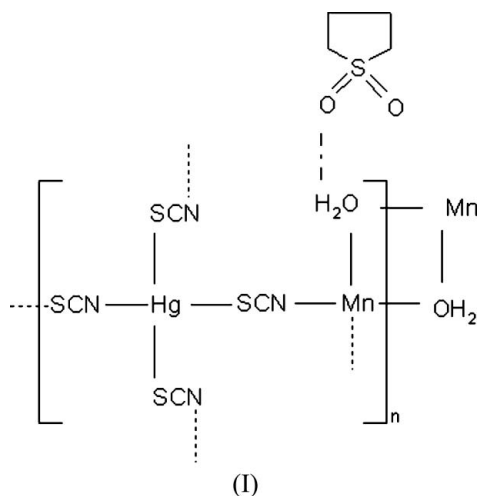


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity. The dotted line indicates the intramolecular hydrogen bond. [Symmetry code: (A) $-x + 2, -y, -z + 1$.]

Deformed $\text{MnN}(\text{SCN})_4\text{O}(\text{H}_2\text{O})_2$ octahedra and $\text{HgS}(\text{SCN})_4$ tetrahedra are formed in the *N,N*-dimethylacetamide (DMA) adduct, $\{[\text{MnHg}(\text{SCN})_4(\text{H}_2\text{O})_2] \cdot 2\text{C}_4\text{H}_9\text{NO}\}_n$ (MMTWD; Wang *et al.*, 2002), in which the DMA molecule is involved in hydrogen bonding with the coordinated water. In the present work, the coordination geometry of the title sulfolane adduct, (I) (MMTWS), is somewhat similar to that of MMTWD and obviously different from that of the other reported LB adducts.



According to the hard and soft acid and base (HSAB) concept (Pearson, 1963, 1966; Balarew & Duhlew, 1984), the harder LB ligands (GME, DMSO, NMF and urea possessing a smaller size and higher electronegativity) are coordinated to the harder Mn^{II} atom *via* their O atoms, while the softer LB ligand TU (lower electronegativity of the S atom) is coordinated to the softer Hg^{II} atom. Because DMA and sulfolane are both medium LB (larger size, higher electronegativity of the O atom), in both structures, the harder H_2O is coordinated to the harder Mn^{II} , and DMA and sulfolane connect to H_2O through hydrogen bonds. However, since sulfolane is larger in size than DMA, the orientation of the two water molecules are intramolecular in the structure of MMTWD, but intermolecular in that of MMTWS.

In MMTWS, each Mn^{II} or Hg^{II} atom is in a distorted $\text{N}(\text{SCN})_4\text{O}(\text{H}_2\text{O})_2$ octahedral or $\text{S}(\text{SCN})_4$ tetrahedral geometry, respectively. The Mn–N and Mn–O bond lengths are somewhat longer and much longer, respectively, than the sum of the ionic radii (2.13 and 2.02 Å, respectively; Shannon, 1976). The bond angles for O1–Mn1–O1^i , N–Mn–N , N–Mn–O and N–Mn–O^i [symmetry code: (i) $-x + 2, -y, -z + 1$] (between adjacent atoms) are obviously different from 90° . The remaining three bond angles, N3–Mn1–N4 , N2–Mn1–O1 and N1–Mn1–O1^i , are much smaller than 180° . The Mn^{II} and water O atoms, and their neighbouring Mn^{II} and $\text{O}(\text{H}_2\text{O})$ atoms, join together to form a parallelogram. This is a particularly interesting feature among the reported MMTC LB adducts.

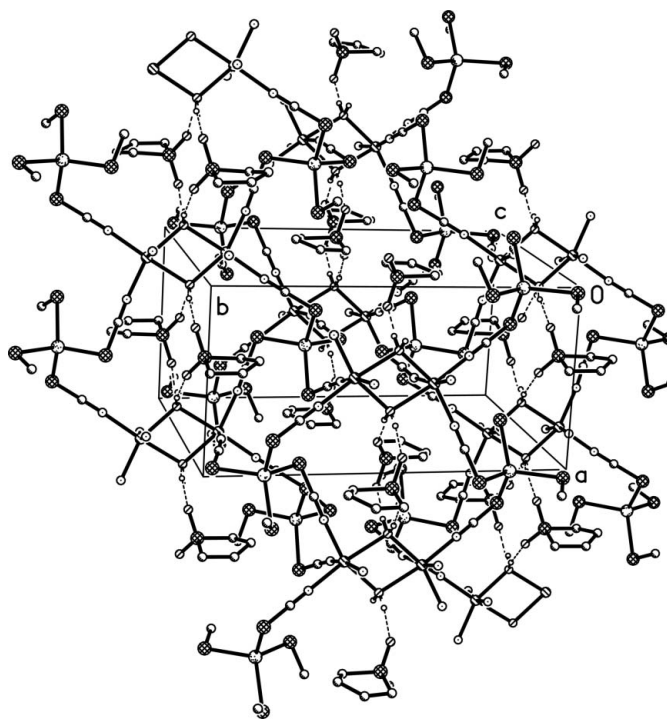


Figure 2
A packing diagram for (I), showing the three-dimensional network. The dashed lines indicate the hydrogen bonds.

The Hg–S bonds of (I) are a little longer than the sum of the single-bond covalent radii (2.52 Å; Pauling, 1960). The bond angles for S–Hg–S deviate from the typical tetrahedral angle.

Experimental

To a crystalline powder of MMTC (2.518 g) was added a mixed solvent of water (10 ml) and sulfolane (2 ml). This mixture was heated and stirred until the MMTC dissolved at about 333 K. The solution was allowed to stand at about 313 K. After several hours, the crystals used for structure analysis were obtained from this solution.

Crystal data

$[\text{MnHg}(\text{NCS})_4(\text{H}_2\text{O})] \cdot \text{C}_4\text{H}_8\text{O}_2\text{S}$
 $M_r = 626.03$
 Monoclinic, $P2_1/n$
 $a = 8.6605$ (9) Å
 $b = 17.1620$ (18) Å
 $c = 12.1745$ (13) Å
 $\beta = 92.034$ (9)°
 $V = 1808.4$ (3) Å³

$Z = 4$
 $D_x = 2.299$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 9.77$ mm⁻¹
 $T = 296$ (2) K
 Prism, colourless
 $0.20 \times 0.10 \times 0.10$ mm

Data collection

Bruker *P4* diffractometer
 ω scans
 Absorption correction: ψ scan
 (*XSCANS*; Siemens, 1996)
 $T_{\text{min}} = 0.315$, $T_{\text{max}} = 0.376$
 4825 measured reflections
 3752 independent reflections

2500 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 $\theta_{\text{max}} = 26.5^\circ$
 3 standard reflections
 every 97 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.072$
 $S = 0.98$
 3752 reflections
 209 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.0266P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.11 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.94 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXTL*
 (Bruker, 1997)
 Extinction coefficient: 0.00342 (14)

Table 1

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

C1–N1	1.142 (10)	N3–Mn1	2.189 (6)
C1–S1	1.661 (9)	N4–Mn1	2.190 (6)
C2–N2 ⁱ	1.152 (9)	O1–Mn1	2.274 (6)
C2–S2	1.643 (8)	O1–Mn1 ^{iv}	2.384 (6)
C3–N3 ⁱⁱ	1.138 (9)	O2–S5	1.419 (7)
C3–S3	1.658 (7)	O3–S5	1.426 (6)
C4–N4 ⁱⁱⁱ	1.139 (9)	S1–Hg1	2.542 (2)
C4–S4	1.659 (8)	S2–Hg1	2.535 (2)
N1–Mn1	2.161 (7)	S3–Hg1	2.546 (2)
N2–Mn1	2.151 (7)	S4–Hg1	2.551 (2)
N1–C1–S1	177.5 (8)	N1–Mn1–N4	92.0 (3)
N2 ⁱ –C2–S2	179.4 (8)	N3–Mn1–N4	167.4 (3)
N3 ⁱⁱ –C3–S3	174.7 (8)	N2–Mn1–O1	156.8 (2)
N4 ⁱⁱⁱ –C4–S4	177.3 (8)	N1–Mn1–O1	103.4 (3)
C1–N1–Mn1	171.6 (7)	N3–Mn1–O1	84.1 (2)
C2 ^v –N2–Mn1	171.9 (6)	N4–Mn1–O1	84.2 (2)
C3 ^{vi} –N3–Mn1	158.9 (7)	N2–Mn1–O1 ^{iv}	84.7 (2)
C4 ^{vii} –N4–Mn1	162.8 (7)	N1–Mn1–O1 ^{iv}	167.9 (2)
Mn1–O1–Mn1 ^{iv}	106.6 (2)	N3–Mn1–O1 ^{iv}	81.9 (2)
C1–S1–Hg1	95.0 (3)	N4–Mn1–O1 ^{iv}	99.2 (2)
C2–S2–Hg1	93.8 (3)	O1–Mn1–O1 ^{iv}	73.4 (2)
C3–S3–Hg1	103.4 (3)	S2–Hg1–S1	112.17 (8)
C4–S4–Hg1	97.6 (3)	S2–Hg1–S3	106.30 (8)
N2–Mn1–N1	99.5 (3)	S1–Hg1–S3	110.86 (10)
N2–Mn1–N3	100.5 (3)	S2–Hg1–S4	110.82 (8)
N1–Mn1–N3	86.2 (2)	S1–Hg1–S4	105.65 (7)
N2–Mn1–N4	92.1 (2)	S3–Hg1–S4	111.12 (9)
Mn1 ^{iv} –O1–Mn1–O1 ^{iv}	0.0		

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

Table 2

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1–H1A \cdots O2 ^{viii}	0.75 (8)	2.01 (8)	2.745 (9)	168 (9)
O1–H1B \cdots O3	0.79 (10)	1.88 (10)	2.660 (8)	166 (9)

Symmetry code: (viii) $-x + 1, -y, -z + 1$.

All H atoms of the sulfolane solvent were placed in geometrically calculated positions and refined using a riding model, with C–H = 0.97 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The two water H atoms were located in a difference map and refined independently with isotropic displacement parameters. The highest peak and deepest hole are located 0.83 and 0.32 \AA , respectively, from atom S3.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Balarew, C. & Duhlew, R. (1984). *J. Solid State Chem.* **55**, 1–10.
- Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell University Press.
- Pearson, R. G. (1963). *J. Am. Chem. Soc.* **85**, 3533–3539.
- Pearson, R. G. (1966). *Science*, **151**, 172–177.
- Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–767.
- Siemens (1996). *XSCANS*. Version 2.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Wang, X.-Q., Yu, W. T., Xu, D., Lu, M. K. & Yuan, D. R. (2000). *Acta Cryst.* **C56**, 418–420.
- Wang, X. Q., Yu, W. T., Xu, D., Lu, M. K. & Yuan, D. R. (2002). *Acta Cryst.* **C58**, m36–m38.
- Wang, X.-Q., Yu, W.-T., Xu, D., Lu, M.-K., Yuan, D.-R., Liu, J.-R. & Lu, G.-T. (2000). *Acta Cryst.* **C56**, 1305–1307.
- Wang, X.-Q., Yu, W. T., Xu, D., Lu, M. K., Yuan, D. R. & Lu, G. T. (2000). *Acta Cryst.* **C56**, 647–648.
- Yan, Y. X., Fang, Q., Yuan, D. R., Tian, Y. P., Liu, Z., Wang, X. M., Jiang, M. H., Williams, D., Siu, A. & Cai, Z. K. (1999). *Chin. Chem. Lett.* **10**, 257–260.
- Yu, W.-T., Wang, X.-Q., Xu, D., Lu, M.-K. & Yuan, D.-R. (2001). *Acta Cryst.* **C57**, 145–146.