

## Polymeric diaquatetra- $\mu$ -thiocyanato-manganese(II)mercury(II) bis(*N,N*-dimethylacetamide) solvate

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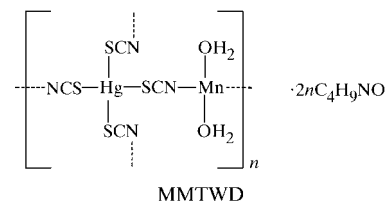
In the title complex,  $\{[\text{MnHg}(\text{SCN})_4(\text{H}_2\text{O})_2] \cdot 2\text{C}_4\text{H}_9\text{NO}\}_n$ , each Mn atom is octahedrally coordinated to four equatorial thiocyanate N atoms and two axial water O atoms. The Mn atom and two O atoms lie on a twofold axis. Two kinds of crystallographically independent Hg atoms (denoted Hg1 and Hg2) are tetrahedrally coordinated with four thiocyanate S atoms and each Hg atom lies on a  $\bar{4}$  axis. *N,N*-Dimethylacetamide molecules are connected to coordinated water molecules through hydrogen bonds. Each pair of Mn and Hg atoms is bridged *via* one thiocyanate ion. An  $\text{Mn}_2\text{Hg}_1\text{Hg}_2(\text{SCN})_4$  16-membered ring is formed as a unit and the four metal atoms are in a chair-form tetrahedral arrangement. The units are linked with one another and form infinite two-dimensional networks.

### Comment

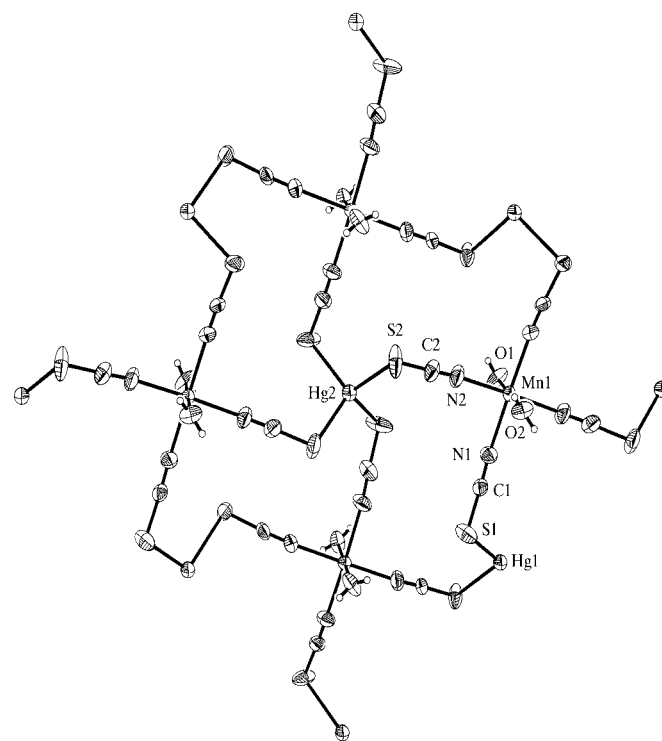
Recently, organometallic materials have been attracting a great deal of attention in the field of non-linear optics (Xu *et al.*, 1994; Wang, 1996; Tian *et al.*, 1997). As for organic materials, organometallic compounds offer the advantages of structural diversity and chemical flexibility, ease of fabrication and tailoring. In addition, an important aspect of utilizing organometallic structures for non-linear optics is their unique charge-transfer capability associated with charge-transfer transitions either from metal to ligand or ligand to metal. The metal–ligand bonding in organometallics gives rise to large molecular hyperpolarizabilities due to the transfer of electron density between the metal atom and the conjugated ligand systems. In addition, the density of the central metal atoms, oxidation states, their size, and the nature of ligands help in tailoring materials with optimized non-linear optical (NLO) interactions. Simultaneously, like inorganic materials, organometallic compounds also possess excellent transmittancy, and temporal and thermal non-linear optical stability (Long, 1995; Jiang & Fang, 1999).

As a ligand with potential S and N donors, the thiocyanate (SCN) ion is interesting not only because of the structural

chemistry of its multifunction coordination modes (Turco & Pecile, 1961), but also because of the formation of complexes with non-linear optical activities (Bergman *et al.*, 1970; Sturmer & Deserno, 1970; Yuan *et al.*, 1997; Xu *et al.*, 1999; Tian *et al.*, 1999; Hellwig *et al.*, 1999). Manganese mercury thiocyanate (MMTC) and its derivatives are potentially useful candidates of organometallic systems (Yan *et al.*, 1999; Wang,



Yu, Xu, Lu & Yuan, 2000; Wang, Yu, Xu, Lu, Yuan & Lu, 2000) because they all contain  $-\text{S}=\text{C}=\text{N}-$  bridges which connect Mn and Hg atoms, forming infinite two-dimensional or three-dimensional networks. These infinite networks confer relatively large polarization, which induces relatively great macroscopic non-linearity for this sort of material. The title compound (MMTWD) is the *N,N*-dimethylacetamide (DMA) adduct of MMTC and is a new NLO crystal. The two DMA molecules are not coordinated to any metal atoms directly, but are involved in hydrogen bonding acting as hydrogen-bond acceptors with two coordinated water molecules acting as hydrogen-bond donors. Such special structural features of the new crystal result in better characteristics than those of MMTC, such as very easy crystal growth and shorter cutoff wavelength.



**Figure 1**

The molecular structure of MMTWD showing 50% probability displacement ellipsoids. H atoms and solvate molecules have been omitted for clarity.

The hard and soft acids and bases concept rationalizes that hard cations show a pronounced affinity for coordination with harder ligands while soft cations prefer coordination with softer ligands (Pearson, 1966; Balarew & Duhlew, 1984; Ozutsmi *et al.*, 1989). The ambidentate SCN ion which is usually S-bonded to a soft and N-bonded to a hard metal centre can also act as a bridging bidentate ligand to satisfy the coordination number of the metal ion. In this structure, the hard  $Mn^{2+}$  is coordinated by the harder N (SCN) and O ( $H_2O$ ) atoms, and the soft  $Hg^{2+}$  is coordinated by the softer S (SCN) atom. The  $Mn^{2+}$  is hexacoordinated and is in an octahedral geometry where four SCN N atoms are coordinated equatorially, and two water molecules combine with Mn through axial O atoms along the *c* axis directions. The  $Mn^{2+}$  atom and two O atoms lie on a twofold axis. The average Mn–N and Mn–O bond lengths are 2.224 and 2.181 Å, respectively, which are typical for octahedral  $Mn^{II}$ . The bond angles for N–Mn–N (between adjacent N atoms) and N–Mn–O lie in the ranges 88.9 (3)–90.7 (3) and 85.0 (3)–95.0 (3)°, with average values of 89.8 and 90.0°, respectively. The O–Mn–O angle is 180°. The Mn–N–C angles, 166.7 (9) and 165.6 (10)°, are significantly less than 180°.

Two kinds of crystallographically independent  $Hg^{2+}$  are coordinated with four SCN S atoms in a tetrahedral geometry, and each of them lies on a  $\bar{4}$  axis (Fig 1). The tetrahedron around Hg2 is regular, while that around Hg1 is deformed. Although the Hg1–S bond lengths are normal, the S–Hg1–S angles, 103.61 (7) and 121.96 (16)°, are far from the typical tetrahedral angle. The N–C–S angles, 176.4 (9) and 177.9 (9)°, are slightly less than 180°. The hydrogen bonding also plays an important role in the crystal packing. All in all, the octahedral geometry of the Mn core and the tetrahedral geometry of the Hg core are both slightly distorted from regular forms. At the same time, the most striking features are the  $-S=C=N-$  bridges which connect Mn and Hg, forming another kind of infinite two-dimensional network (Figs. 1

and 2). The macroscopic non-linear susceptibility may be related to microscopic hyperpolarizabilities of the dipolar SCN ions and the deformed  $MnN_4O_2$  octahedra and  $HgS_4$  tetrahedra. Such a new special infinite three-dimensional network donates a large polarization, which in turn, we believe, induces a great macroscopic non-linearity (Zyss & Ledoux, 1994). The second harmonic generation (SHG) effect of the crystals was studied by the power SHG effect technique (Kurtz & Perry, 1968) and was found to be comparable with potassium dihydrogen phosphate (KDP).

### Experimental

To a crystalline powder of MMTc (20 g, 41 mmol) was added about 100 ml of a mixed solvent of water and DMA (1:1, v/v); the pH of the solution was adjusted to 3 by the addition of hydrochloric acid. This mixture was heated and stirred until MMTc dissolved. The slightly pale-red solution was allowed to stand in an oven at 303 K. After one day, the colourless crystals used for X-ray structure analysis were obtained from this solution.

#### Crystal data

[MnHg(SCN) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> C <sub>4</sub> H <sub>9</sub> NO	Mo K $\alpha$ radiation
<i>M<sub>r</sub></i> = 698.17	Cell parameters from 35 reflections
Tetragonal, $P\bar{4}$	$\theta = 5.053$ – $14.433^\circ$
<i>a</i> = 12.2436 (6) Å	$\mu = 7.232$ mm <sup>-1</sup>
<i>c</i> = 8.0708 (6) Å	<i>T</i> = 293 (2) K
<i>V</i> = 1209.86 (12) Å <sup>3</sup>	Tetragonal, colourless
<i>Z</i> = 2	0.35 × 0.30 × 0.25 mm
<i>D<sub>x</sub></i> = 1.916 Mg m <sup>-3</sup>	

#### Data collection

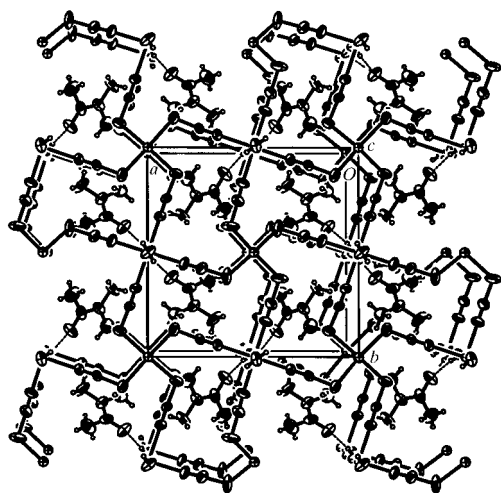
Bruker P4 diffractometer	<i>R</i> <sub>int</sub> = 0.027
$\theta/2\theta$ scans	$\theta_{max}$ = 29.98°
Absorption correction: $\psi$ scans (XSCANS; Bruker, 1996)	<i>h</i> = -1 → 17
<i>T</i> <sub>min</sub> = 0.094, <i>T</i> <sub>max</sub> = 0.164	<i>k</i> = -1 → 17
2684 measured reflections	<i>l</i> = -1 → 11
1891 independent reflections (plus 593 Friedel equivalents)	3 standard reflections every 97 reflections
1859 reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	intensity decay: none

**Table 1**

Selected geometric parameters (Å, °).

Hg1–S1	2.536 (2)	O3–C3	1.247 (10)
Hg2–S2	2.525 (3)	N1–C1	1.139 (8)
Mn1–O1	2.152 (6)	N2–C2	1.139 (9)
Mn1–O2	2.209 (6)	N3–C3	1.304 (10)
Mn1–N2	2.211 (7)	N3–C5	1.452 (9)
Mn1–N1	2.236 (6)	N3–C6	1.455 (9)
S1–C1	1.671 (8)	C3–C4	1.523 (13)
S2–C2	1.643 (9)		
S1–Hg1–S1 <sup>i</sup>	103.61 (7)	C1–S1–Hg1	98.3 (3)
S1–Hg1–S1 <sup>ii</sup>	121.96 (16)	C2–S2–Hg2	100.8 (4)
S2 <sup>iii</sup> –Hg2–S2	109.32 (8)	C1–N1–Mn1	166.7 (9)
S2–Hg2–S2 <sup>iv</sup>	109.78 (17)	C2–N2–Mn1	165.6 (10)
O1–Mn1–N2	95.0 (3)	C3–N3–C5	116.8 (7)
O2–Mn1–N2	85.0 (3)	C3–N3–C6	122.2 (9)
N2–Mn1–N2 <sup>v</sup>	170.0 (5)	C5–N3–C6	120.4 (7)
O1–Mn1–N1 <sup>v</sup>	92.0 (3)	N1–C1–S1	176.4 (9)
O2–Mn1–N1 <sup>v</sup>	88.0 (3)	N2–C2–S2	177.9 (9)
N2–Mn1–N1 <sup>v</sup>	90.7 (3)	O3–C3–N3	121.7 (9)
N2–Mn1–N1	88.9 (3)	O3–C3–C4	121.0 (8)
N1 <sup>v</sup> –Mn1–N1	175.9 (5)	N3–C3–C4	117.1 (8)

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



**Figure 2**

The crystal packing of MMTWD viewed down the *c* axis. Hydrogen bonds are indicated by dashed lines.

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.076$   
 $S = 1.035$   
 2484 reflections  
 137 parameters  
 H atoms treated by a mixture of  
 independent and constrained  
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.0296P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.78 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.71 \text{ e } \text{Å}^{-3}$   
 Extinction correction: *SHELXTL*  
 (Bruker, 1997)  
 Extinction coefficient: 0.0093 (4)  
 Absolute structure: Flack (1983)  
 Flack parameter = 0.04 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O1-H1 \cdots O3^i$	0.86 (9)	1.98 (10)	2.820 (7)	166 (11)
$O2-H2 \cdots O3^{ii}$	0.86 (8)	1.94 (7)	2.754 (7)	158 (7)

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

H atoms bonded to C atoms were treated as riding atoms, with a C—H distance of 0.96 Å. The water H atoms were located from difference Fourier maps and the distances between them were restrained in the refinement.

Data collection: *XSCANS* (Bruker, 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: GD1102). Services for accessing these data are described at the back of the journal.

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