Acta Crystallographica Section C
**Crystal Structure Communications**
ISSN 0108-2701

# Poly[bis(*N*-methylformamide)-tetra-$\mu$-thiocyanato-manganese(II)-mercury(II)]

**Xin-Qiang Wang,* Wen-Tao Yu, Dong Xu, Guang-Hui Zhang and Yan-Ling Geng**

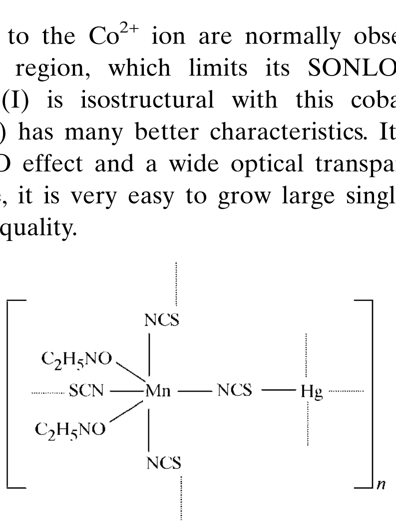
State Key Laboratory of Crystal Materials, Institute of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China
Correspondence e-mail: xqwang@icm.sdu.edu.cn

Received 22 February 2005
Accepted 6 April 2005
Online 13 May 2005

The title complex, $[MnHg(NCS)_4(C_2H_5NO)_2]_n$, consists of slightly distorted $MnN_4O_2$ octahedra and $HgS_4$ tetrahedra. Each $Mn^{II}$ cation is bound to four N atoms of the NCS groups and two O atoms of the *N*-methylformamide (NMF) ligands in a *cis* configuration. Each $Hg^{II}$ cation is coordinated to four S atoms of NCS groups. Each pair of $Mn^{II}$ and $Hg^{II}$ cations is connected by an –NCS– bridge, forming an infinite three-dimensional –Mn—NCS—Hg– network.

## Comment

Versatile and efficient sources of blue–violet or UV light are of fundamental importance for many applications, such as high-density optical data storage, medical diagnosis, photolithography, underwater communications, laser displays, *etc*. To date, second-order non-linear optical (SONLO) materials capable of efficient frequency conversion of IR or visible laser radiation to visible or UV wavelengths are of considerable interest in these fields (Zhang *et al.*, 2004). Materials with large second-order optical non-linearities, transparency at all wavelengths involved and stable physicochemical performance (thermal and temporal stability) are needed in order to realise many of these applications. Manganese mercury thiocyanate (MMTC) (Yan *et al.*, 1999) and quite a few of its Lewis-base adducts (Wang, Yu, Xu, Lu & Yuan, 2000; Wang, Yu, Xu, Lu, Yuan & Lu, 2000; Wang, Yu, Xu, Lu, Yuan, Liu & Lu, 2000; Yu *et al.*, 2001) have been found to crystallize in acentric structures. All of them exhibit good SONLO effects and a wide transparency wavelength region. In a continuation of this work, a novel compound, (I), the *N*-methylformamide (NMF) adduct of MMTC, has been prepared. The crystal structure of the NMF adduct of cobalt mercury thiocyante, bis(*N*-methylformamide)tetrakis(thiocyanato)cobalt(II)mercury(II), was reported nearly 20 years ago (Kinoshita & Ouchi, 1986). It crystallizes in a non-centrosymmetric space group, but unfortunately the low energy *d*–*d* transitions present due to the $Co^{2+}$ ion are normally observed in the visible light region, which limits its SONLO usefulness. Compound (I) is isostructural with this cobalt complex. However, (I) has many better characteristics. It possesses a high SONLO effect and a wide optical transparency range. Furthermore, it is very easy to grow large single crystals of high optical quality.



(I)

According to the hard and soft acids and bases (HSAB) concept (Pearson, 1966; Balarew & Duhlew, 1984), the harder metals show a pronounced affinity for coordination with harder ligands, while softer metals prefer coordination with softer ligands. In the structure of (I), each hard $Mn^{II}$ cation is hexacoordinated by four hard NCS ligands *via* their N atoms and two hard NMF ligands *via* their O atoms in a slightly distorted octahedral geometry and each osfter $Hg^{II}$ cation is tetracoordinated by four soft NCS ligands *via* their S atoms in a slightly distorted tetragonal geometry.

In compound (I), the two O atoms of the NMF ligands coordinate to the $Mn^{II}$ cation in a *cis* configuration. However, in the similar structure of the DMSO adduct (DMSO is dimethyl sulfoxide; Wang, Yu, Xu, Lu & Yuan, 2000), two O atoms of the DMSO ligands coordinate to the $Mn^{II}$ cation in a *trans* configuration. This difference is due to the smaller size of NMF compared with DMSO. In (I), each $Mn^{II}$ cation is bound to four N atoms belonging to NCS groups and two O atoms of

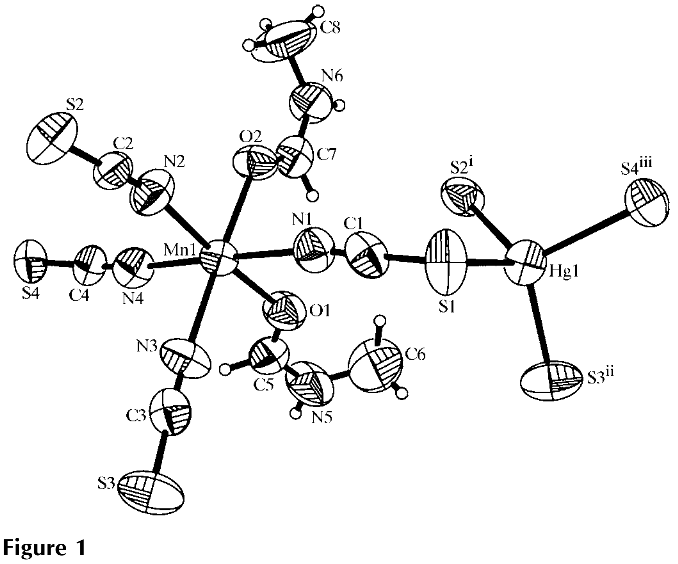


**Figure 1**
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z$; (ii) $x - \frac{1}{2}, \frac{3}{2} - y, z$; (iii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z$.]

DOI: 10.1107/S0108270105010814

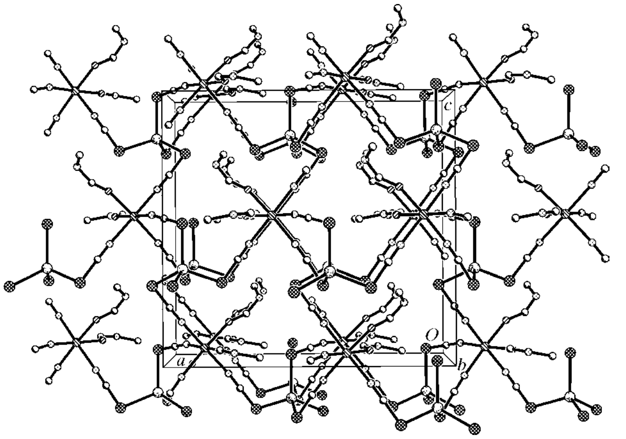


**Figure 2**
A packing diagram for (I), showing the three-dimensional network.

NMF ligands. The resulting hexacoordinate environment of $Mn^{II}$ exhibits slight distortions from ideal octahedral. The Mn—N [2.199 (12)–2.240 (12) Å] and Mn—O [2.178 (9) and 2.176 (9) Å] bond lengths are all much larger than the sums of the ionic radii (2.13 and 2.02 Å, respectively; Shannon, 1976).

Each $Hg^{II}$ cation, coordinated to four NCS S atoms, has a tetrahedral geometry. The tetrahedron is also slightly deformed. The Hg—S bond lengths are in the range 2.526 (4)–2.563 (4) Å, with an average of 2.543 Å, a little larger than the sum of the single-bond covalent radii (2.52 Å; Pauling, 1960). The S—Hg—S bond angles [101.65 (14)–117.21 (16)°] deviate markedly from the typical tetrahedral angle.

The C—N—Mn angles [164.8 (12)–175.5 (12)°] are close to 180°, while the C—S—Hg angles [94.2 (4)–97.1 (5)°] are much smaller than 180° and exhibit significant bending. The C—N and C—S bond lengths are slightly smaller than the accepted triple-bond length of 1.16 Å and the normal single C—S bond length of 1.81 Å, respectively (Akers *et al.*, 1968). The NCS groups are quasi-linear [N—C—S angles 176.7 (13)–179.0 (13)°].

The striking feature of this type of complex is the –NCS– bridge, which connects the two metals to form infinite two- or three-dimensional networks; a three-dimensional network is formed in (I).

The macroscopic non-linear susceptibility of the crystal of (I) may be related to the microscopic hyperpolarizabilities of the dipolar $NCS^-$ ions, and to the octupolar distorted $MnN_4O_2$ octahedra and $HgS_4$ tetrahedra (Zyss & Ledoux, 1994). The second harmonic generation (SHG) effect of the crystals has been studied (Kurtz & Perry, 1968) and found to be nearly the same as that of urea. The optical transmission of a crystal of (I) was measured using a Hitachi U-3500 spectrophotometer; it was found that the transparency range is 365–2920 nm.

## Experimental

An NMF solution (5 ml) of MMTC (4.41 g, 9 mmol) was added slowly to water (25 ml) with stirring at room temperature. After a while, compound (I) precipitated. The crystals used for the X-ray structure analysis were obtained from a mixed solvent of NMF and water (1:3 *v*/*v*) using a temperature-lowering method.

*Crystal data*

$[MnHg(NCS)_4(C_2H_5NO)_2]$
$M_r = 605.99$
Orthorhombic, $Pna2_1$
$a = 16.1203\ (15)$ Å
$b = 7.7373\ (7)$ Å
$c = 15.2135\ (18)$ Å
$V = 1897.5\ (3)$ Å$^3$
$Z = 4$
$D_x = 2.121$ Mg m$^{-3}$

Mo $K\alpha$ radiation
Cell parameters from 43 reflections
$\theta = 6.4$–$12.5°$
$\mu = 9.20$ mm$^{-1}$
$T = 293\ (2)$ K
Prism, colourless
$0.23 \times 0.18 \times 0.13$ mm

*Data collection*

Bruker *P*4 diffractometer
$\omega$ scans
Absorption correction: $\psi$ scan (*XSCANS*; Siemens, 1996)
$T_{min} = 0.10$, $T_{max} = 0.30$
2951 measured reflections
2417 independent reflections
1656 reflections with $I > 2\sigma(I)$

$R_{int} = 0.030$
$\theta_{max} = 27.5°$
$h = -1 \rightarrow 20$
$k = -1 \rightarrow 10$
$l = -19 \rightarrow 1$
3 standard reflections every 97 reflections intensity decay: none

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.077$
$S = 0.98$
2417 reflections
203 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.68$ e Å$^{-3}$
$\Delta\rho_{min} = -0.56$ e Å$^{-3}$
Extinction correction: *SHELXTL* (Bruker, 1997)
Extinction coefficient: 0.00286 (17)
Absolute structure: Flack (1983), with 162 Friedel pairs
Flack parameter: 0.12 (2)

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

| | | | |
|---|---|---|---|
| C1—N1 | 1.140 (15) | N2—Mn1 | 2.214 (12) |
| C1—S1 | 1.649 (14) | N3—Mn1 | 2.199 (12) |
| C2—N2 | 1.144 (14) | N4—Mn1 | 2.240 (12) |
| C2—S2 | 1.625 (13) | O1—Mn1 | 2.178 (9) |
| C3—N3 | 1.136 (16) | O2—Mn1 | 2.176 (9) |
| C3—S4 | 1.655 (15) | S1—Hg1 | 2.526 (4) |
| C4—N4 | 1.127 (15) | S2—Hg1$^{i}$ | 2.548 (4) |
| C4—S3 | 1.641 (14) | S3—Hg1$^{ii}$ | 2.563 (4) |
| N1—Mn1 | 2.233 (12) | S4—Hg1$^{iii}$ | 2.534 (5) |
| | | | |
| N1—C1—S1 | 179.0 (13) | O2—Mn1—N1 | 86.6 (4) |
| N2—C2—S2 | 178.8 (13) | O1—Mn1—N1 | 88.2 (4) |
| N3—C3—S4 | 176.7 (13) | N3—Mn1—N1 | 89.5 (5) |
| N4—C4—S3 | 178.1 (12) | N2—Mn1—N1 | 90.0 (4) |
| C1—N1—Mn1 | 171.3 (12) | O2—Mn1—N4 | 93.5 (4) |
| C2—N2—Mn1 | 164.8 (12) | O1—Mn1—N4 | 89.3 (4) |
| C3—N3—Mn1 | 175.5 (12) | N3—Mn1—N4 | 90.4 (4) |
| C4—N4—Mn1 | 171.5 (13) | N2—Mn1—N4 | 92.4 (4) |
| C1—S1—Hg1 | 95.2 (5) | N1—Mn1—N4 | 177.5 (4) |
| C2—S2—Hg1 | 97.1 (5) | S1—Hg1—S3$^{iv}$ | 117.21 (16) |
| C4—S3—Hg1 | 94.2 (4) | S1—Hg1—S2$^{v}$ | 109.83 (15) |
| C3—S4—Hg1 | 95.5 (5) | S3$^{iv}$—Hg1—S2$^{v}$ | 104.46 (15) |
| O2—Mn1—O1 | 87.8 (4) | S1—Hg1—S4$^{vi}$ | 101.65 (14) |
| O2—Mn1—N3 | 176.0 (4) | S3$^{iv}$—Hg1—S4$^{vi}$ | 109.72 (16) |
| O1—Mn1—N3 | 93.0 (4) | S2$^{v}$—Hg1—S4$^{vi}$ | 114.40 (14) |
| O2—Mn1—N2 | 88.3 (4) | C2—S2—Hg1$^{i}$ | 97.1 (5) |
| O1—Mn1—N2 | 175.8 (4) | C3—S3—Hg1$^{ii}$ | 95.5 (5) |
| N3—Mn1—N2 | 90.7 (5) | C4—S4—Hg1$^{iii}$ | 94.2 (4) |

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z$; (ii) $x + \frac{1}{2}, -y + \frac{3}{2}, z$; (iii) $-x + \frac{3}{2}, y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $x - \frac{1}{2}, -y + \frac{3}{2}, z$; (v) $x - \frac{1}{2}, -y + \frac{1}{2}, z$; (vi) $-x + \frac{3}{2}, y - \frac{1}{2}, z + \frac{1}{2}$.

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N5—H5*B*···O2$^{vii}$ | 0.86 | 2.49 | 3.285 (19) | 154 |

Symmetry codes: (vii) $x, y + 1, z$.

All H atoms were placed in geometrically calculated positions, with C—H distances in the range 0.93–0.96 Å and N—H distances of 0.86 Å, and refined using a riding model, with $U_{\rm iso}(H) = 1.2U_{\rm eq}(C,N)$, or $1.5U_{\rm eq}(C)$ for $CH_3$ groups.

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

This work was supported by an '863' grant (No. 2002 A A313070) of the National Advanced Materials Committee of China (NAMCC) and grants (Nos. 60476020, 50272037 and 60377016) of the National Natural Science Foundation of China (NNSFC).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1235). Services for accessing these data are described at the back of the journal.

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