metal-organic compounds

Manganese mercury thiocyanate (MMTC) glycol monomethyl ether

Xin-Qiang Wang,* Wen-Tao Yu, Dong Xu, Meng-Kai Lu, Duo-Rong Yuan and Guang-Tian Lu

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

In the title complex, $[MnHg(NCS)_4(C_3H_8O_2)]_n$, each Hg atom is tetrahedrally coordinated with four S atoms of the SCN^- ions, and each Mn atom is octahedrally coordinated with four N atoms of the SCN^- ions, one hydroxyl O atom and one ethereal O atom of the glycol monomethyl ether molecule. Each pair of Hg and Mn atoms is bridged by one SCN^- ion. A 24-membered $Mn_3Hg_3(SCN)_6$ ring is formed as the strucrural unit, with the six metal atoms in a chair-form hexagonal arrangement. The units are condensed and linked three-dimensionally in the crystal resulting in a diamond-like structure.

Comment

This work is part of a research project concerning the investigation of the second-order optical non-linearities of double-metal thiocyanates and their derivatives. Over the past several years, the investigation of organometallic and coordination complexes for useful non-linear optical (NLO) materials has been a very active field, because such materials have the potential for combining the high optical non-linearity and chemical flexibility of organics with the physical ruggedness of inorganics (Xu *et al.*, 1993; Long, 1995; Jiang & Fang, 1999). According to the idea of 'combining the inorganic distorted polyhedron with asymmetric conjugate organic molecules',

(I)
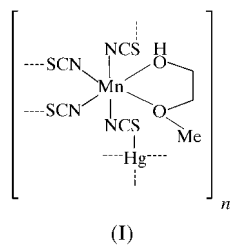
many new metal–organic NLO crystals have been found (Xu *et al.*, 1987, 1994, 1999; Hou *et al.*, 1993; Yuan *et al.*, 1997; Tian *et al.*, 1999). The manganese mercury tetrathiocyanate crystal $[MnHg(SCN)_4$, MMTC] was reported previously (Yan *et al.*,

1999) and shows high second harmonic intensity. The title compound, (I), is the glycol monomethyl ether (GME) adduct of MMTC and is a new NLO crystal. The properties of the new crystal have some better characteristics than those of MMTC, such as being very easy to grow as large-size crystals, processing of pyroelectric effect *etc.*

The HSAB (hard and soft acids and bases) concept (Pearson, 1963, 1966; Balarew & Duhlew, 1984; Yamaguchi *et al.*, 1985; Ozutsmi *et al.*, 1989) rationalizes that the hard Mn^{2+} is coordinated with the harder N (SCN) and O (GME) atoms, and the soft Hg^{2+} is coordinated with the softer S (SCN) atom. The Hg^{2+} is coordinated with four SCN S atoms and has a
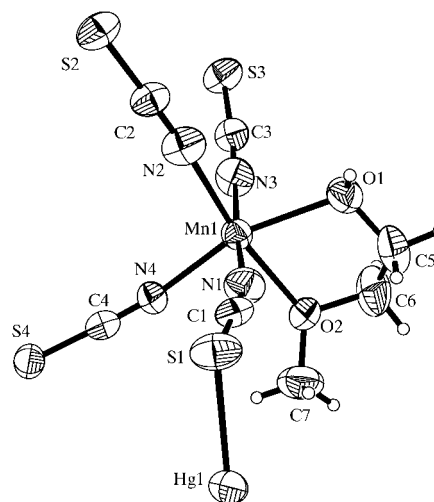

Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

tetrahedral geometry. The Mn^{2+} is hexacoordinated and has an octahedral geometry; the GME molecule combines with Mn as a bidentate ligand through two O atoms of the hydroxyl and ethereal groups, while four SCN N atoms are bonded to the remaining positions. The Hg—S lengths are unexceptional. The S—Hg—S bond angles vary somewhat from ideal tetrahedral geometry. The Hg—S—C bond angles are all close to 97°. The average Mn—N and Mn—O bond lengths are 2.190 and 2.251 Å, respectively. In total, the tetrahedral geometry of the mercury core and the octahedral geometry of the manganese core are sightly deformed from the ideal forms. The most striking feature of the structure is the formation of the SCN bridges which connect Mn and Hg, forming an infinite three-dimensional network. The macroscopic non-linear susceptibility may be related to microscopic hyperpolarizabilities of the dipolar SCN^- ions, as in MMTC, and distorted HgS_4 tetrahedra and MnN_4O_2 octahedra (Zyss, 1991). Such a new special infinite three-dimensional network donates a large polarization, which in turn, we believe, induces a great macroscopic non-linearity. The second harmonic generation (SHG) effect of the crystals has been studied (Kurtz & Perry, 1968) and found to be comparable to that of urea.
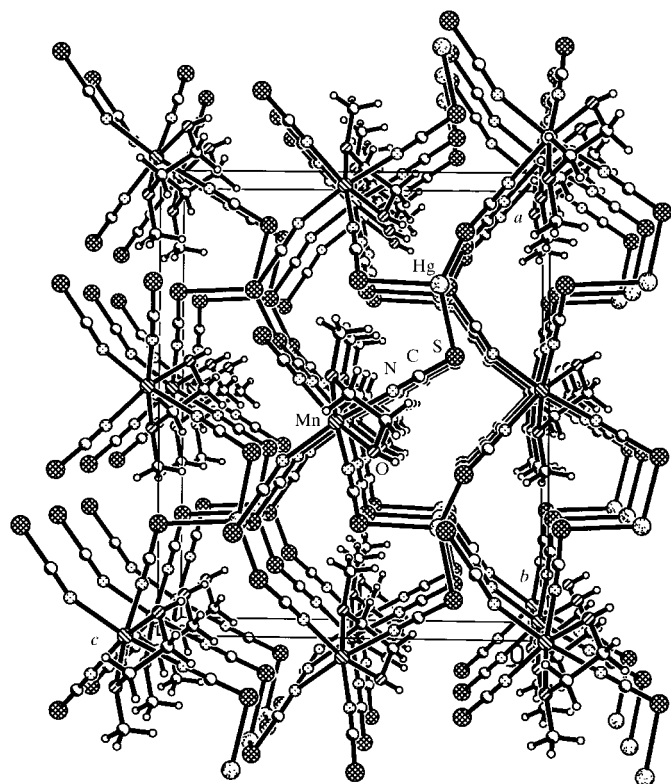
metal-organic compounds

Figure 2
The packing diagram of (I).

Experimental

To a crystalline powder of MMTC (7.81 g, 16.0 mmol) was added about 12 ml of a mixed solvent of GME and water (v/v = 5:7). This mixture was heated and stirred until the MMTC dissolved. The solution, which was slightly pale red, was left standing at about 293 K. The deposited crystals were separated. The crystals used for the X-ray structure analysis were obtained from a more dilute solution of the mixed solvent which had been allowed to stand overnight.

Crystal data

$[MnHg(NCS)_4(C_3H_8O_2)]$	Mo $K\alpha$ radiation
$M_r = 563.94$	Cell parameters from 36
Orthorhombic, $Pca2_1$	reflections
$a = 16.2046 (16)$ Å	$\theta = 4.82–14.83°$
$b = 7.2974 (5)$ Å	$\mu = 10.912$ mm^{-1}
$c = 13.5090 (14)$ Å	$T = 293 (2)$ K
$V = 1597.5 (3)$ Å^3	Prism, pale green
$Z = 4$	$0.25 \times 0.20 \times 0.18$ mm
$D_x = 2.345$ Mg m^{-3}	

Data collection

Bruker $P4$ diffractometer	$R_{int} = 0.047$
$\omega/2\theta$ scans	$\theta_{max} = 28°$
Absorption correction: ψ scans	$h = -21 \rightarrow 1$
(*XSCANS*; Siemens, 1996)	$k = -1 \rightarrow 9$
$T_{min} = 0.076, T_{max} = 0.140$	$l = -17 \rightarrow 1$
2634 measured reflections	3 standard reflections
2149 independent reflections	every 97 reflections
1779 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0590P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.101$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.041$	$\Delta\rho_{max} = 1.92$ e Å^{-3}
2149 reflections	$\Delta\rho_{min} = -0.95$ e Å^{-3}
173 parameters	Extinction correction: *SHELXTL*97
H atoms constrained	(Bruker, 1997)
	Extinction coefficient: 0.0044 (4)

H atoms were treated as riding with O—H = 0.82, C—H(methyl) = 0.96 and C—H(CH$_2$) = 0.97 Å.

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*.

Table 1
Selected geometric parameters (Å, °).

Hg1—S4^i	2.479 (3)	Mn1—N2	2.174 (11)
Hg1—S1	2.506 (3)	Mn1—N1	2.200 (10)
Hg1—S3^{ii}	2.536 (4)	Mn1—N3	2.215 (10)
Hg1—S2^{iii}	2.685 (4)	Mn1—O1	2.247 (8)
Mn1—N4	2.169 (9)	Mn1—O2	2.255 (7)
S4^i—Hg1—S1	117.52 (10)	S4^i—Hg1—S2^{iii}	105.87 (10)
S4^i—Hg1—S3^{ii}	120.00 (10)	S1—Hg1—S2^{iii}	103.53 (11)
S1—Hg1—S3^{ii}	108.35 (10)	S3^{ii}—Hg1—S2^{iii}	98.31 (11)

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

References

Balarew, C. & Duhlew, R. (1984). *J. Solid State Chem.* **55**, 1–10.
Bruker (1997). *SHELXTL.* Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Hou, W.-B., Jiang, M.-H., Yuan, D.-R., Xu, D., Zhang, N., Liu, M.-G. & Tao, X.-T. (1993). *Mater. Res. Bull.* **28**, 645–653.
Jiang, M. H. & Fang, Q. (1999). *Adv. Mater.* **11**, 1147–1151.
Kurtz, S. K. & Perry, T. T. (1968). *J. Appl. Phys.* **39**, 3798–3813.
Long, N. J. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 21–38.
Ozutsmi, K., Takamuku, T., Ishiguro, S. & Ohraki, H. (1989). *Bull. Chem. Soc. Jpn*, **62**, 1875–1879.
Pearson, R. G. (1963). *J. Am. Chem. Soc.* **85**, 3533–3548.
Pearson, R. G. (1966). *Science*, pp. 172–177.
Siemens (1996). *XSCANS User's Manual.* Version 2.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Tian, Y.-P., Yu, W.-T., Fang, Q., Wang, X.-Q., Yuan, D.-R., Xu, D. & Jiang, M.-H. (1999). *Acta Cryst.* C**55**, 1393–1395.
Xu, D., Jiang, M.-H., Tao, X.-T. & Shao, Z.-S. (1987). *J. Synth. Cryst.* **16**, 1–7.
Xu, D., Liu, M.-G., Hou, W.-B., Yuan, D.-R. & Jiang, M.-H. (1994). *Mater. Res. Bull.* **29**, 73–79.
Xu, D., Yu, W.-T., Wang, X.-Q., Yuan, D.-R., Lu, M.-K., Yang, P., Guo, S.-Y., Meng, F.-Q. & Jiang, M.-H. (1999). *Acta Cryst.* C**55**, 1203–1205.
Xu, D., Yuan, D.-R., Zhang, N., Hou, W.-B., Liu, M.-G., Sun, S.-Y. & Jiang, M.-H. (1993). *J. Phys. D*, **26**, B230–235.
Yamaguchi, T., Yamamoto, K. & Ohtaki, H. (1985). *Bull. Chem. Soc. Jpn*, **58**, 3235–3241.
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.
Yuan, D.-R., Xu, D., Fang, Q., Yu, W.-T. & Jiang, M.-H. (1997). *Appl. Phys. Lett.* **70**, 544–546.
Zyss, J. (1991). *Non-Linear Opt.* **1**, 1–18.