metal-organic compounds

Poly[[bis(dimethyl sulfoxide-κO)tris-(thiocyanato-κN)manganese(II)]-μ-thiocyanato-$\kappa^2 N$:S-mercury(II)]

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In the title complex, $[MnHg(SCN)_4(C_2H_6SO)_2]_n$, 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
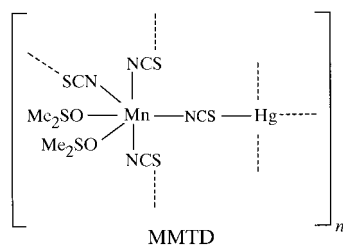
molecular engineering and the double-ligand model (Xu *et al.*, 1987, 1994, 1999; Tao *et al.*, 1987; Zhang *et al.*, 1989; Yuan *et al.*, 1990, 1997; Yu *et al.*, 1991; Hou *et al.*, 1993; Wang, 1996; Tian *et al.*, 1997). The compound manganese mercury tetrathiocyanate, $MnHg(SCN)_4$ (MMTC), was reported 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 Mn^{2+} and Co^{2+} show a pronounced affinity for coordination with harder ligands, while soft cations such as Cd^{2+} and Hg^{2+} prefer coordination with softer ligands (Pearson, 1963, 1966; Balarew & Duhlew, 1984; Yamaguchi *et al.*, 1985; Ozutsmi *et al.*, 1989). In the structure of MMTD, the hard Mn^{2+} ion is coordinated with the harder N (SCN) and O (DMSO) ligands, while the soft Hg^{2+} ion is coordinated with the softer S (SCN) ligands.

The Hg^{2+} ion is coordinated with four SCN S atoms and is in a tetrahedral geometry. The 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 managanese(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)°.
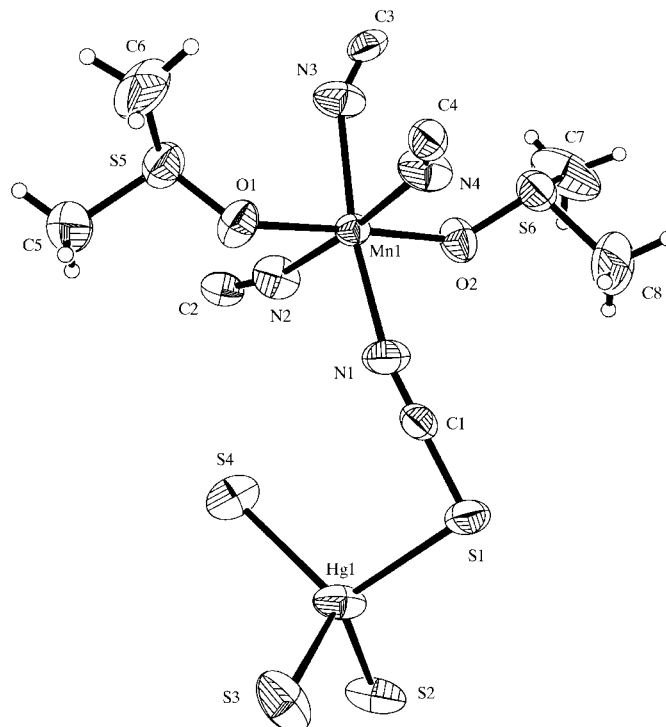

Figure 1
The molecular structure of MMTD showing 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

Overall, the tetrahedral geometry of the Hg core and the octahedral geometry of the Mn core are both sightly deformed from the ideal forms. The most striking features are the $-S=C=N-$ 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 HgS_4 tetrahedra and MnN_4O_2 octahedra (Zyss, 1991). What is more, the average Mn—N—C bond angle is 156.1°, which is significantly different from 180°; 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 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.
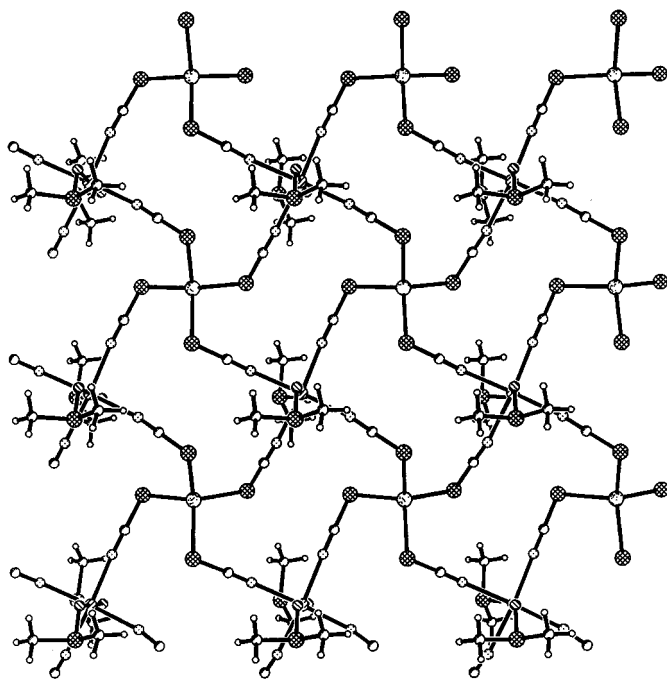

Figure 2
Packing diagram for MMTD showing the two-dimensional network.

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

$[MnHg(SCN)_4(C_2H_6SO)_2]$	Mo $K\alpha$ radiation
$M_r = 644.11$	Cell parameters from 35
Orthorhombic, $P2_12_12_1$	reflections
$a = 8.4937\,(6)$ Å	$\theta = 5.73–12.96°$
$b = 8.5226\,(4)$ Å	$\mu = 8.849$ mm^{-1}
$c = 27.884\,(4)$ Å	$T = 293\,(2)$ K
$V = 2018.5\,(3)$ Å^3	Orthorhombic, colourless
$Z = 4$	$0.25 \times 0.22 \times 0.20$ mm
$D_x = 2.120$ Mg m^{-3}	

Data collection

Bruker $P4$ diffractometer	$R_{int} = 0.035$
$\omega/2\theta$ scans	$\theta_{max} = 27.5°$
Absorption correction: ψ scan	$h = -1 \rightarrow 11$
($XSCANS$; Siemens, 1996)	$k = -1 \rightarrow 11$
$T_{min} = 0.119$, $T_{max} = 0.165$	$l = -1 \rightarrow 36$
3460 measured reflections	3 standard reflections
2659 independent reflections (plus	every 97 reflections
572 Friedel-related reflections)	intensity decay: none
2310 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.043$	$\Delta\rho_{max} = 0.96$ e Å^{-3}
$wR(F^2) = 0.112$	$\Delta\rho_{min} = -1.40$ e Å^{-3}
$S = 1.027$	Extinction correction: $SHELXTL$
3231 reflections	(Bruker, 1997)
200 parameters	Extinction coefficient: 0.0045 (2)
H-atom parameters constrained	Absolute structure: Flack (1983)
$w = 1/[\sigma^2(F_o{}^2) + (0.0513P)^2$	Flack parameter = 0.004 (12)
$+ 2.4486P]$	
where $P = (F_o{}^2 + 2F_c{}^2)/3$	

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^i	178.7 (10)
N2—Mn1—N1	94.4 (3)	N3—C3—S2^{ii}	177.9 (10)
O2—Mn1—N4	95.1 (3)	N4—C4—S4^{iii}	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^{-3} 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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