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Tetrathioureamercury(II) tetrathiocyanatomanganate(II)

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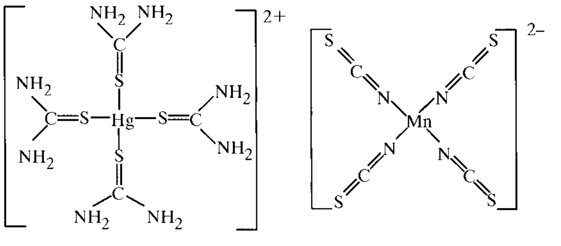
In the title complex, $[Hg(CH_4N_2S)_4][Mn(NCS)_4]$, the Hg and Mn atoms sit at special positions with $\overline{4}$ symmetry and are tetrahedrally coordinated to four thiourea (TU) S and four thiocyanate (SCN) N atoms, respectively. The structure consists of discrete cationic and anionic $[Hg(TU)_4]^{2+}$ and $[Mn(SCN)_4]^{2-}$ complexes, and weak $N_{TU}—H\cdots S_{SCN}$ hydrogen-bond bridges exist between these complexes.

Comment

During the last few years, organic non-linear optical (NLO) crystals have attracted much interest due to their superior properties over inorganic NLO materials, such as higher susceptibility, faster response and the capability of designing components on the molecular level. However, unlike inorganic NLO crystals, they have not come into wide use, owing to drawbacks such as the difficulty of growing large perfect single crystals, poor physicochemical stability and difficulties in cutting and polishing the devices. Under these circumstances, crystals of complexes of organometallic materials with NLO effects have been developed which are expected not only to retain high NLO effects, but also to minimize some of the shortcomings of pure organic crystals; in other words, they have the advantages of both organic and inorganic crystals in terms of their physicochemical properties. This approach has resulted in their practical use in frequency-doubling of laser radiation (Long, 1995; Jiang & Fang, 1999).



(I)

Transition metal thiourea (TU) and thiocyanate (SCN) coordination complexes are potentially useful candidates for such organometallic systems. As ligands with potential S and N donors, the TU molecule and the SCN ion are interesting not only because of the structural chemistry of their multifunctional coordination modes, but also because of the possibility of formation of organometallic coordination complexes with NLO activities (Xing *et al.*, 1987; Bhat & Dharmaprakash, 1998; Sturmer & Deserno, 1970; Yuan *et al.*, 1997). It would be even more interesting if these two ligands were both present in one compound and this compound were to possess good NLO properties. The crystal structure of $[Hg(CH_4N_2S)_4][Co(NCS)_4]$, (II), was reported in the 1960s (Korczynski & Porai-Koshits, 1965). It crystallizes in a noncentrosymmetric space group, but unfortunately the low energy *d*–*d* transitions present in (II) due to the Co^{2+} ion are normally observed in the visible light region and so limit its NLO usefulness. The title compound, (I), is isostructural with

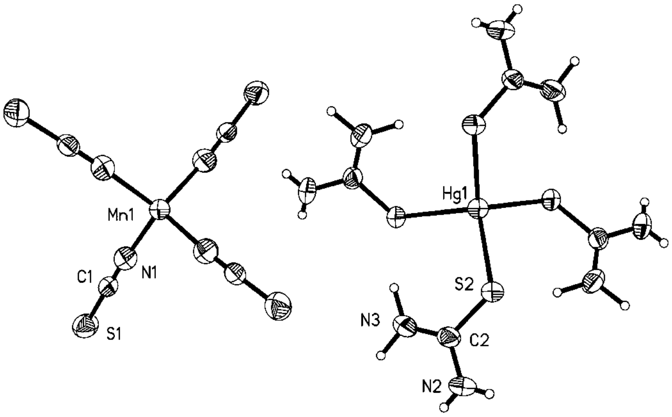


Figure 1
The molecular structure of (I) showing the atom-labelling scheme and 50% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii.

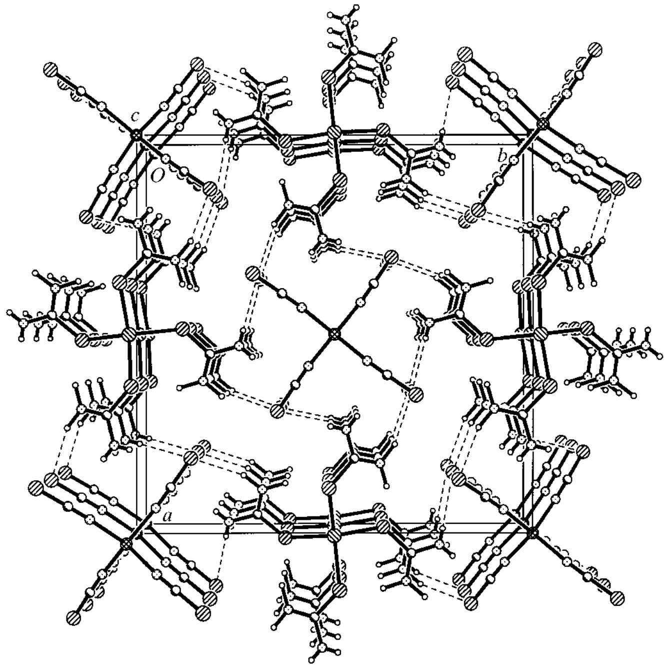


Figure 2
The packing for (I) viewed down the *c* axis.

(II). However, the new crystal has far better characteristics than those of (II), such as a relatively high non-linearity and a greater ease of growing into large single crystals.

The concept of hard and soft acids and bases rationalizes that soft cations show a pronounced affinity for coordination with the softer ligands, while hard cations prefer coordination with harder ligands (Pearson, 1966; Balarew & Duhlew, 1984). In the structure of (I) (Fig. 1), the soft Hg^{2+} ion is coordinated by the softer S (TU), while the hard Mn^{2+} ion is coordinated by the harder N (SCN). Neither of them is coordinated by the medium S (SCN).

Both of the metal cations in (I) are tetracoordinated and in a tetrahedral environment. Although all the Hg—S and Mn—N bond lengths are 2.576 (2) and 2.083 (12) Å, respectively, the bond angles for S—Hg—S and N—Mn—N range from 106.81 (4) to 114.94 (8)°, and from 105.5 (4) to 117.8 (10)°, respectively, which obviously deviate from typical tetrahedral angles. The TU molecules and the SCN ions are linked by N—H···S hydrogen bonds to form a three-dimensional network in space (Fig. 2).

In short, the tetrahedral geometries of the Hg and Mn cores in (I) are both slightly distorted from the regular forms. The macroscopic non-linear susceptibility may be related to microscopic hyperpolarizabilities of the polarizable TU molecules, the dipolar SCN ions and the deformed HgS_4 and MnN_4 tetrahedra, which are connected *via* N—H···S hydrogen bonds. These factors result in a large polarization, which in turn, we believe, induces a large macroscopic non-linearity (Zyss & Ledoux, 1994). The second harmonic generation (SHG) effect of the crystals was measured by the powder SHG technique (Kurtz & Perry, 1968) and was found to be somewhat superior to that of urea crystals.

Experimental

To an aqueous solution (20 ml) containing $MnHg(SCN)_4$ (5.2 g, 10.7 mmol), thiourea (4.2 g, 13.8 mmol) was added; the pH of the solution was adjusted to 3 by adding hydrochloric acid. This mixture was heated and stirred until the $MnHg(SCN)_4$ had dissolved. The aqueous solution was then allowed to stand at room temperature. After a few hours, colourless crystals of (I) suitable for X-ray structure analysis were obtained.

Crystal data

$[Hg(CH_4N_2S)_4][Mn(NCS)_4]$
$M_r = 792.32$
Tetragonal, $I\bar{4}$
$a = 17.4297\ (8)$ Å
$c = 4.1754\ (3)$ Å
$V = 1268.46\ (12)$ Å^3
$Z = 2$
$D_x = 2.074$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 36 reflections
$\theta = 4.69–12.60°$
$\mu = 7.223$ mm^{-1}
$T = 293\ (2)$ K
Block, colourless
0.26 × 0.22 × 0.20 mm

Data collection

Bruker *P*4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*XSCANS*; Siemens, 1996)
$T_{min} = 0.181$, $T_{max} = 0.236$
1492 measured reflections
1374 independent reflections
1337 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 29.95°$
$h = -24 \rightarrow 1$
$k = -24 \rightarrow 1$
$l = -5 \rightarrow 1$
3 standard reflections every 97 reflections intensity decay: none

Table 1
Selected geometric parameters (Å, °).

Hg1—S2	2.5762 (16)	C2—N3	1.291 (10)
Mn1—N1	2.083 (12)	C2—N2	1.324 (8)
C1—N1	1.141 (13)	C2—S2	1.729 (7)
C1—S1	1.627 (7)		
$S2^i$—Hg1—S2	106.81 (4)	N3—C2—N2	119.2 (6)
S2—Hg1—$S2^{ii}$	114.94 (8)	N3—C2—S2	124.5 (5)
$N1^{iii}$—Mn1—$N1^{iv}$	117.8 (10)	N2—C2—S2	116.2 (6)
$N1^{iii}$—Mn1—N1	105.5 (4)	C1—N1—Mn1	174.7 (12)
N1—C1—S1	178.6 (10)	C2—S2—Hg1	110.5 (3)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*B*···$S1^i$	0.86	2.73	3.584 (8)	175
N3—H3*A*···$S1^{ii}$	0.86	2.68	3.515 (7)	163
N3—H3*B*···$S2^{iii}$	0.86	2.54	3.322 (8)	152

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.080$
$S = 1.051$
1374 reflections
68 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.118P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.70$ e Å^{-3}
$\Delta\rho_{min} = -1.02$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.008 (11)

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: SK1404). Services for accessing these data are described at the back of the journal.

References

Balarew, C. & Duhlew, R. (1984). *J. Solid State Chem.* **55**, 1–10.
Bhat, S. G. & Dharmaprakash, S. M. (1998). *Mater. Res. Bull.* **33**, 833–840.
Bruker (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Jiang, M. H. & Fang, Q. (1999). *Adv. Mater.* **11**, 1147–1151.
Korczynski, A. & Porai-Koshits, M. A. (1965). *Rocz. Chem.* **39**, 1567.
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.
Pearson, R. G. (1966). *Science*, pp. 172–177.
Siemens (1996). *XSCANS*. Version 2.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sturmer, W. & Deserno, U. (1970). *Phys. Lett. A*, **32**, 539–540.
Xing, G. C., Jiang, M. H., Shao, Z. S. & Xu, D. (1987). *Chin. Phys. Lett.* **14**, 302–308.
Yuan, D. R., Xu, D., Fang, Q., Yu, W. T. & Jiang, M. H. (1997). *Appl. Phys. Lett.* **70**, 544–546.
Zyss, J. & Ledoux, I. (1994). *Chem. Rev.* **94**, 77–105.

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