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Poly[[[tri(urea-κO)manganese(II)]-μ-thiocyanato-$\kappa^2 N$:S-mercury(II)]-tri-μ-tetrathiocyanato]

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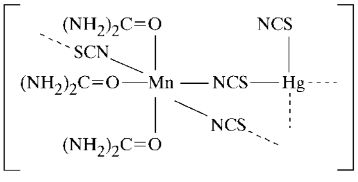
The title complex, $[MnHg(SCN)_4(CH_4N_2O)_3]_n$, consists of slightly distorted octahedral MnN_3O_3 and tetrahedral HgS_4 units. The Mn^{II} atom is coordinated by the O atoms of three urea molecules and by the N atoms of three SCN^- ions; Hg^{II} is coordinated by four S atoms from SCN^- ions. Each pair of Mn^{II} and Hg^{II} atoms is connected by an –SCN– bridge, forming infinite two-dimensional –Mn—NCS—Hg– networks.

Comment

Owing to the diverse applications of coordination compounds in chemistry–physics and technology, there is continuing interest in the synthesis and characterization of such compounds, especially those of transition metals. In these studies, the supramolecular architecture of multi-dimensional networks is one of the most attractive aspects from the technological point of view because these networks may have electronic, magnetic, optical or catalytic applications (Batten & Robson, 1998). For designing infinite inorganic and organic frameworks, various pseudo-halide and pseudo-chalocogenide ions, such as CN^-, OCN^-, SCN^-, $SeCN^-$, CNO^-, N^{3-}, CN_2^{2-} and SN_2^{2-}, and complementary ligands are used (Kitazawa *et al.*, 1994; Cortes *et al.*, 1997; Munno *et al.*, 1997; Wang *et al.*, 2000; Nandibewoor *et al.*, 2000; Thirumaran & Ramalingam, 2000; Becker & Jansen, 2001). Due to their versatility in acting as monodentate, bidentate or bridging ligands, multi-dimensional framework structures linking alternately one metal atom (M) to another (M') could be built using pseudo-halide or pseudo-chalocogenide ions.

The coordination chemistries of transition metals have been extensively studied from both a chemical and structural point of view, because of their ability to adopt different modes of coordination determined by considerations of size, as well as electrostatic and covalent bonding forces. The presence of pseudo-halide and pseudo-chalocogenide ions introduces some additional degrees of freedom.

As part of these investigations, the title compound, (I), the urea adduct of manganese mercury thiocyanate, $MnHg(SCN)_4$ (Yan *et al.*, 1999), has been prepared, in which SCN^- ions act as bridging ligands [linking manganese(II) and mercury(II)] and urea molecules act as complementary ligands.



(I)

According to the hard and soft acid 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 this structure, each harder Mn^{II} atom is hexacoordinated *via* harder 3(NCS) + 3(urea-O) in a slightly distorted octahedral geometry, and each softer Hg^{II} atom is tetracoordinated *via* softer 4(SCN) in a slightly distorted tetragonal geometry.

The Mn—N [range 2.225 (5)–2.243 (5) Å] and Mn—O [range 2.152 (3)–2.197 (4) Å] bond lengths are both much longer than the sum of the Shannon (1976) ionic radii, *i.e.* 2.13 and 2.02 Å, respectively. This is probably because the assumed valences of the N and O atoms are not appropriate, for the charges on the SCN^- ions and urea molecules are much delocalized. The N—Mn—N, O—Mn—N and O—Mn—O (between adjacent atoms) bond angles are in the ranges 87.2 (2)–88.7 (2), 88.2 (2)–94.8 (2) and 86.18 (14)–91.71 (13)°, with average values of 87.95, 90.82 and 88.95°, respectively, which are somewhat different from the typical octahedral angle of 90°.

The Hg—S bond lengths [range 2.4865 (14)–2.6035 (15) Å; average 2.5473 Å] are much shorter than the sum of the Shannon ionic radii (2.80 Å), a result of the considerable effect of delocalization of the charges on the SCN^- ions. The S—Hg—S bond angles [range 101.84 (5)–126.91 (6)°] deviate greatly from the typical tetrahedral angle.

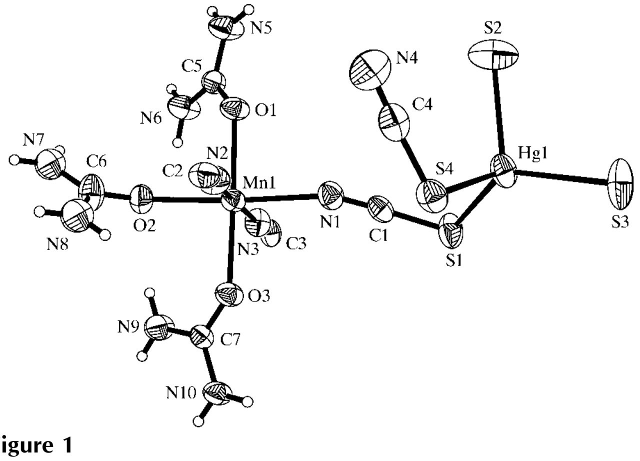


Figure 1
Part of the molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Among the C—S—Hg angles, C1—S1—Hg1 is much larger than the rest. Although the C2—N2—Mn1 [172.0 (4)°] and C3—N3—Mn1 [178.2 (4)°] angles are both close to 180°, that of C1—N1—Mn1 [159.1 (4)°] is smaller and exhibits a significant bending. The SCN groups are quasi-linear [the N—C—S angles are in the range 175.9 (5)–178.4 (5)°], which is the striking feature of these kinds of complexes, *i.e.* where –SCN– bridges connect bimetals forming infinite two- or three-dimensional networks (two-dimensional networks are formed in the present complex).

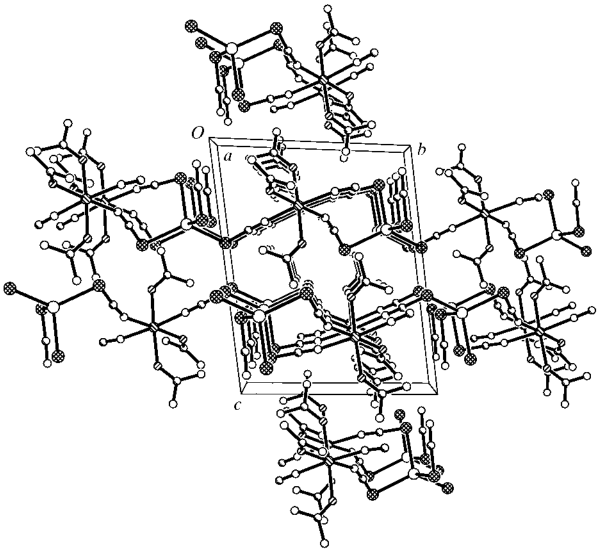


Figure 2
Packing diagram for (I) showing the two-dimensional network.

Table 1
Selected geometric parameters (Å, °).

Hg1—S1	2.4865 (14)	S1—C1	1.653 (6)
Hg1—S3	2.514 (2)	S2—C2^{i}	1.653 (6)
Hg1—S2	2.585 (2)	S3—C3^{ii}	1.667 (6)
Hg1—S4	2.6035 (15)	S4—C4	1.658 (7)
Mn1—O3	2.152 (3)	C1—N1	1.152 (7)
Mn1—O1	2.176 (3)	C2—N2	1.151 (7)
Mn1—O2	2.197 (4)	C2—S2^{iii}	1.653 (6)
Mn1—N3	2.225 (5)	C3—N3	1.146 (7)
Mn1—N2	2.226 (5)	C3—S3^{iv}	1.667 (6)
Mn1—N1	2.243 (5)	C4—N4	1.146 (8)

S1—Hg1—S3	126.91 (6)	O3—Mn1—N1	92.27 (15)
S1—Hg1—S2	108.63 (6)	O1—Mn1—N1	89.8 (2)
S3—Hg1—S2	105.24 (8)	O2—Mn1—N1	175.6 (2)
S1—Hg1—S4	101.84 (5)	N3—Mn1—N1	88.7 (2)
S3—Hg1—S4	103.95 (5)	N2—Mn1—N1	87.2 (2)
S2—Hg1—S4	109.38 (6)	C1—S1—Hg1	99.2 (2)
O3—Mn1—O1	177.20 (13)	C2^{i}—S2—Hg1	97.1 (2)
O3—Mn1—O2	91.71 (13)	C3^{ii}—S3—Hg1	97.0 (2)
O1—Mn1—O2	86.18 (14)	C4—S4—Hg1	97.0 (2)
O3—Mn1—N3	88.2 (2)	N1—C1—S1	175.9 (5)
O1—Mn1—N3	89.9 (2)	N2—C2—S2^{iii}	178.3 (5)
O2—Mn1—N3	89.5 (2)	N3—C3—S3^{iv}	178.4 (5)
O3—Mn1—N2	89.3 (2)	N4—C4—S4	176.7 (6)
O1—Mn1—N2	92.8 (2)	C1—N1—Mn1	159.1 (4)
O2—Mn1—N2	94.8 (2)	C2—N2—Mn1	172.0 (4)
N3—Mn1—N2	175.1 (2)	C3—N3—Mn1	178.2 (4)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N10—H10A···O3^{i}	0.86	2.15	2.964 (5)	159

Symmetry code: (i) $-1-x, 1-y, 1-z$.

Experimental

$MnHg(SCN)_4$ was prepared by the reaction of MnX_2, HgX_2 (where X = Cl, NO_3 or CH_3COO) and ASCN (where A = K, Na or NH_4) (molar ratio 1:1:4) in water. The crystalline powders of $MnHg(SCN)_4$ and urea were dissolved in water in a stoichiometric ratio. The mixture was then left to stand for several days, whereupon crystals of (I) were obtained.

Crystal data

$[MnHg(SCN)_4(CH_4N_2O)_3]$
$M_r = 668.04$
Triclinic, $P\overline{1}$
$a = 7.5210$ (7) Å
$b = 10.6669$ (9) Å
$c = 13.3202$ (9) Å
$\alpha = 80.185$ (6)°
$\beta = 82.009$ (7)°
$\gamma = 75.147$ (7)°
$V = 1012.69$ (14) Å^3
$Z = 2$
$D_x = 2.191$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 53 reflections
$\theta = 4.7$–14.5°
$\mu = 8.64$ mm^{-1}
$T = 293$ (2) K
Prism, pale green
0.31 × 0.21 × 0.20 mm

Data collection

Bruker $P4$ diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (*XSCANS* ; Bruker, 1996)
$T_{min} = 0.125$, $T_{max} = 0.179$
4448 measured reflections
3561 independent reflections
3229 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 25°$
$h = -8 \rightarrow 1$
$k = -12 \rightarrow 12$
$l = -15 \rightarrow 15$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.065$
$S = 1.04$
3558 reflections
236 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0255P)^2 + 2.0461P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max} = 0.84$ e Å^{-3}
$\Delta\rho_{min} = -0.81$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0064 (3)

Atoms N7 and N8 are disordered. Atoms N7, N7′, N8 and N8′ were refined isotropically and their site-occupation factors were 0.59, 0.41, 0.69 and 0.31, respectively. H atoms were placed geometrically (N—H = 0.86 Å) and refined using a riding model, with $U_{iso} = 1.2U_{eq}$(parent atom).

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: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1045). Services for accessing these data are described at the back of the journal.

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