Polymeric bis(N,N-dimethyl-acetamide)tetrakis(thiocyanato)-cadmium(II)mercury(II)

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The title complex, $\{[CdHg(SCN)_4(C_4H_9NO)_2]_2\}_n$, contains two crystallographically independent Cd^{II} centres and two Hg^{II} centres. Each Cd^{II} atom is bound to four N atoms belonging to SCN groups and to two O atoms from N,N-dimethylacetamide (DMA) ligands in an octahedral geometry. Each Hg^{II} centre is tetrahedrally coordinated by four SCN S atoms.

Comment

In recent years, the preparation and characterization of infinite two- and three-dimensional networks has spawned much interest, since these networks may have electronic, magnetic, optical or catalytic applications (Batten & Robson, 1998). Various pseudohalide and pseudochalcogenide ions, such as CN^-, OCN^-, SCN^-, $SeCN^-$, $TeCN^-$, CNO^-, N_3^-, CN_2^{2-} and SN_2^{2-}, have been used for designing infinite networks (Cortes et al., 1997; Kitazawa et al., 1994; Yuan et al., 1997; Zhang et al., 2000; Becker & Jansen, 2001). Because of their versatility as monodentate, bidentate or bridging ligands, pseudohalide or pseudochalcogenide ions can be used to build multi-dimensional framework structures connecting one metal atom to another.

(I)
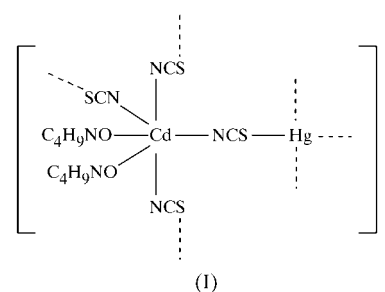
Group IIB metal complexes have been extensively studied, mainly due to the capability of these d^{10} metal ions to adopt
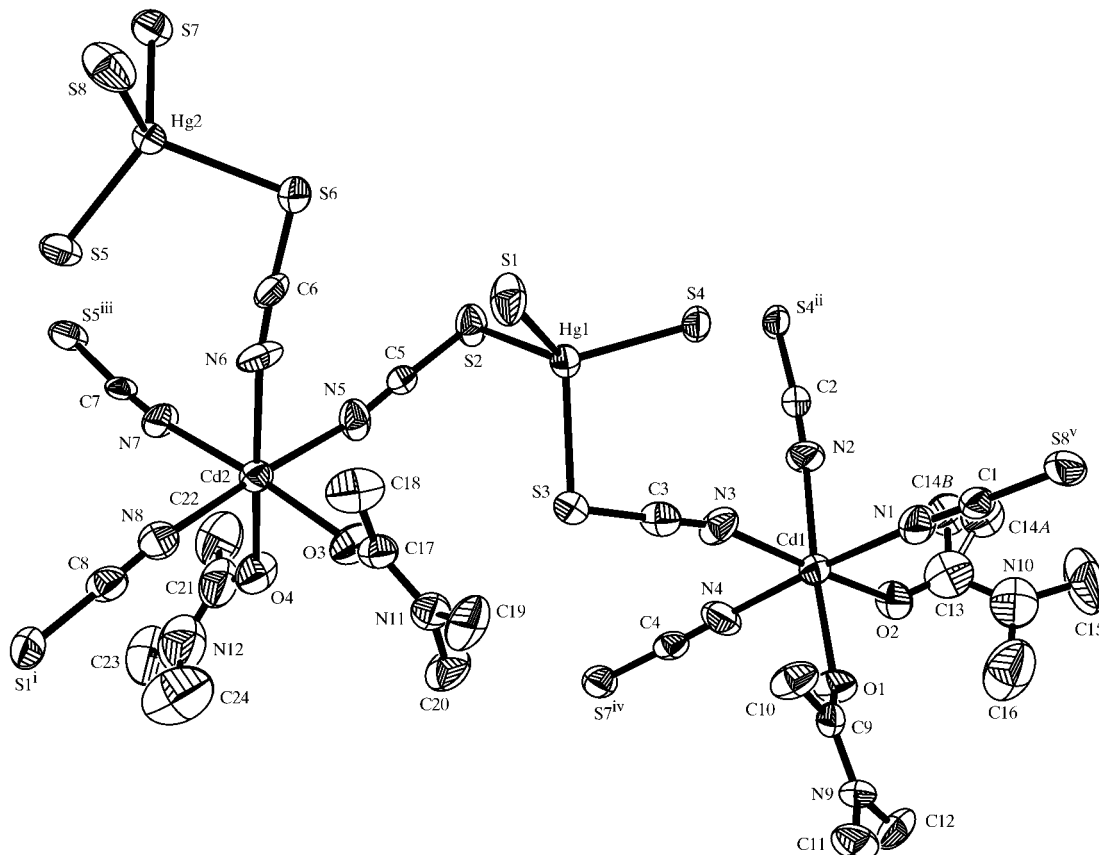
Figure 1
A view of the molecular structure of (I) with 30% probability displacement ellipsoids. H atoms have been omitted for clarity [symmetry codes: (i) x, $1 - y$, $z - \frac{1}{2}$; (ii) $3 - x$, $\frac{3}{2} + y$, $\frac{3}{2} - z$; (iii) $2 - x$, $\frac{3}{2} + y$, $\frac{1}{2} - z$; (iv) $x + 1$, y, z; (v) $x + 1$, $\frac{1}{2} - y$, $z + \frac{1}{2}$].

metal-organic compounds

different modes of coordination, determined by considerations of size, as well as by electrostatic and covalent bonding forces. The presence of pseudohalide and pseudochalcogenide ions introduces some additional degrees of freedom, as seen in the title complex, (I), a novel Lewis base adduct of cadmium mercury thiocyanate (CMTC).

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 Cd^{II} is coordinated by four hard SCN N atoms and two DMA O atoms. Each soft Hg^{II} is coordinated by four of the softer S ligands (SCN). Each Cd^{II} is octahedrally coordinated and each Hg^{II} is tetrahedrally coordinated.

Both Cd^{II} centres exhibit slight distortions from ideal geometry. The Cd1—N bond lengths [2.288 (12)–2.347 (11) Å] are longer than the Cd2—N distances [2.297 (13)–2.339 (10) Å], but all are shorter than the sum of ionic radii (2.41 Å; Shannon, 1976). This is partly because the assumed valence of the N atom is not appropriate, since the charge on the SCN⁻ ion is highly delocalized. The Cd1—O and Cd2—O bond lengths [2.258 (8) and 2.269 (9), and 2.259 (9) and 2.273 (9) Å, respectively] are somewhat shorter than the Cd—N distances. The bond angles (between adjacent atoms) N—Cd1—N, N—Cd2—N, O—Cd1—N and O—Cd2—N are 84.9 (5)–96.2 (4), 82.8 (4)–97.6 (4), 87.4 (4)–100.1 (4) and 85.7 (4)–99.4 (3)°, respectively, with average values of 90.0, 90.2, 90.6 and 90.5°, respectively. The O1—Cd1—O2 and O3—Cd2—O4 angles are 86.7 (3) and 86.5 (3)°, respectively, slightly smaller than the ideal octahedral angle.

Each of the two crystallographically independent Hg^{II} centres is tetrahedrally coordinated by four SCN S atoms. The tetrahedra are slightly deformed, with Hg1—S and Hg2—S bond lengths in the ranges 2.486 (3)–2.558 (4) and 2.502 (3)–2.562 (4) Å, respectively, averaging 2.526 and 2.534 Å, respectively. The former is slightly shorter than the latter, and both are much shorter than the sum of the ionic radii (2.80 Å; Shannon, 1976), also likely due to considerable delocalization of the charge on the SCN⁻ ion. The S—Hg1—S and S—Hg2—S bond angles [104.18 (14)–118.02 (13) and 107.09 (14)–116.80 (13)°, respectively] deviate somewhat from the typical tetrahedral angle.

The average C—S—Hg angle is 97.4°, which is normal compared with CMTC [97.6 (3)°]. Although the C2—N2—Cd1 [172.5 (12)°] and C7—N7—Cd2 [172.1 (10)°] bond angles are similar to those in CMTC [171.3 (8)°], the remaining C—N—Cd bond angles are significantly smaller and exhibit a significant bending. The SCN groups are quasi-linear [N—C—S angles 175.0 (10)–178.8 (15)°], which is the striking feature of these kinds of complexes; the –S=C=N– bridges connecting bimetals, forming infinite two- or three-dimensional networks; a three-dimensional network is formed in (I). This feature is most important, as it confers high physicochemical stability and other desirable properties on these complexes.

Experimental

Crystal data

[CdHg(SCN)₄(C₄H₉NO)₂]₂	$D_x = 2.071$ Mg m⁻³
$M_r = 1439.11$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 39
$a = 14.829$ (3) Å	reflections
$b = 16.1465$ (19) Å	$\theta = 5.1–12.3°$
$c = 19.282$ (3) Å	$\mu = 7.95$ mm⁻¹
$\beta = 91.27$ (2)°	$T = 293$ (2) K
$V = 4615.7$ (12) Å³	Prism, light pink
$Z = 4$	$0.30 \times 0.25 \times 0.20$ mm

Table 1
Selected geometric parameters (Å, °).

Hg1—S4	2.487 (3)	S2—C5	1.642 (14)
Hg1—S1	2.514 (4)	S3—C3	1.631 (14)
Hg1—S3	2.551 (4)	S4—C2ii	1.616 (13)
Hg1—S2	2.557 (4)	S5—C7iii	1.649 (13)
Hg2—S5	2.498 (3)	S6—C6	1.647 (13)
Hg2—S8	2.527 (4)	S7—C4iv	1.640 (14)
Hg2—S6	2.538 (4)	S8—C1v	1.637 (15)
Hg2—S7	2.564 (4)	N1—C1	1.137 (15)
Cd1—O2	2.266 (9)	N2—C2	1.136 (14)
Cd1—O1	2.276 (6)	N3—C3	1.136 (15)
Cd1—N4	2.307 (12)	N4—C4	1.142 (14)
Cd1—N1	2.329 (12)	N5—C5	1.144 (14)
Cd1—N2	2.339 (11)	N6—C6	1.156 (14)
Cd1—N3	2.360 (12)	N7—C7	1.148 (14)
Cd2—O3	2.259 (7)	N8—C8	1.125 (14)
Cd2—O4	2.277 (8)	C1—S8vi	1.637 (15)
Cd2—N7	2.302 (11)	C2—S4ii	1.616 (13)
Cd2—N5	2.308 (12)	C4—S7vii	1.640 (14)
Cd2—N8	2.308 (12)	C7—S5iii	1.649 (13)
Cd2—N6	2.330 (11)	C8—S1viii	1.632 (15)
S1—C8i	1.632 (15)		
S4—Hg1—S1	118.14 (14)	N1—Cd1—N3	96.2 (5)
S4—Hg1—S3	104.62 (12)	N2—Cd1—N3	86.0 (4)
S1—Hg1—S3	108.69 (15)	O3—Cd2—O4	87.3 (3)
S4—Hg1—S2	110.07 (12)	O3—Cd2—N7	174.1 (4)
S1—Hg1—S2	104.23 (14)	O4—Cd2—N7	86.9 (4)
S3—Hg1—S2	111.17 (13)	O3—Cd2—N5	85.5 (4)
S5—Hg2—S8	116.84 (14)	O4—Cd2—N5	89.3 (4)
S5—Hg2—S6	107.87 (12)	N7—Cd2—N5	94.9 (4)
S8—Hg2—S6	107.28 (16)	O3—Cd2—N8	90.7 (4)
S5—Hg2—S7	110.02 (11)	O4—Cd2—N8	90.5 (4)
S8—Hg2—S7	107.14 (15)	N7—Cd2—N8	88.8 (4)
S6—Hg2—S7	107.28 (14)	N5—Cd2—N8	176.2 (4)
O2—Cd1—O1	87.2 (3)	O3—Cd2—N6	99.4 (3)
O2—Cd1—N4	90.2 (4)	O4—Cd2—N6	169.1 (4)
O1—Cd1—N4	87.5 (4)	N7—Cd2—N6	86.5 (4)
O2—Cd1—N1	89.1 (4)	N5—Cd2—N6	82.8 (4)
O1—Cd1—N1	89.2 (4)	N8—Cd2—N6	97.9 (4)
N4—Cd1—N1	176.6 (4)	N1—C1—S8vi	177.0 (17)
O2—Cd1—N2	87.1 (4)	N2—C2—S4ii	175.6 (13)
O1—Cd1—N2	174.0 (4)	N3—C3—S3	177.4 (15)
N4—Cd1—N2	94.3 (4)	N4—C4—S7vii	177.6 (13)
N1—Cd1—N2	89.0 (4)	N5—C5—S2	178.1 (13)
O2—Cd1—N3	171.2 (4)	N6—C6—S6	175.9 (13)
O1—Cd1—N3	99.9 (3)	N7—C7—S5iii	175.9 (12)
N4—Cd1—N3	85.0 (5)	N8—C8—S1viii	179.9 (19)

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

Data collection

Bruker *P*4 diffractometer	$R_{int} = 0.028$
ω scans	$\theta_{max} = 25°$
Absorption correction: ψ scan	$h = -17 \rightarrow 1$
(*XSCANS*; Siemens, 1996)	$k = -1 \rightarrow 19$
$T_{min} = 0.094$, $T_{max} = 0.204$	$l = -22 \rightarrow 22$
9846 measured reflections	3 standard reflections
8130 independent reflections	every 97 reflections
4454 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.054$	$w = 1/[\sigma^2(F_o^2) + (0.0491P)^2]$
$wR(F^2) = 0.121$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} = 0.001$
8127 reflections	$\Delta\rho_{max} = 1.37$ e Å^{-3}
474 parameters	$\Delta\rho_{min} = -0.67$ e Å^{-3}

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*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1215). Services for accessing these data are described at the back of the journal.

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