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Polymeric bis(*N*-methylformamide)tetrathiocyanatocadmium(II)mercury(II)

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The title complex, poly[bis(*N*-methylformamide)tetra-μ-thiocyanatocadmium(II)mercury(II)], $[CdHg(NCS)_4(C_2H_5NO)_2]_n$, contains slightly distorted octahedral CdN_4O_2 and tetrahedral HgS_4. The Cd^{II} atom is coordinated by the N atoms of four SCN groups and O atoms of two *N*-methylformamide ligands in a *cis* orientation. The Hg^{II} atom is coordinated by S atoms of one independent and three symmetry-related SCN groups. The two metal atoms, *viz*. Cd^{II} and Hg^{II}, are connected by an —S=C=N— bridge, forming an infinite three-dimensional network.

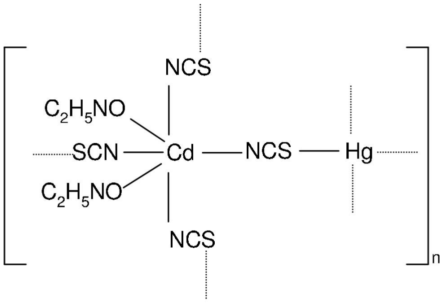
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(N–C) = 0.030 Å
R factor = 0.041
wR factor = 0.081
Data-to-parameter ratio = 10.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Second-order non-linear optical (SONLO) materials capable of efficient frequency conversion of infrared or visible laser radiation to blue–violet or ultraviolet wavelengths are of considerable interest in high-density optical data storage, medical diagnosis, photolithography, underwater communications, laser displays, *etc*. Materials with large second-order optical non-linearities, transparency at all wavelengths involved and stable physicochemical performance are needed in order to realise many of these applications (Long, 1995; Zhang *et al*., 2004).



(I)

Cadmium mercury thiocyanate (CMTC) consists of flattened CdN_4 and HgS_4 tetrahedra (Yuan *et al*., 1997) and its two reported Lewis-base adducts (Zhou *et al*., 2000; Guo *et al*., 2001) consist of distorted CdN_4O_2 octahedra and HgS_4 tetrahedra. All of them exhibit good SONLO effects and wide transparency wavelength regions. To continue this work, the title complex, (I), an *N*-methylformamide (NMF) adduct of CMTC, has been prepared. The crystal structure of an NMF adduct of cobalt mercury thiocyanate, bis(*N*-methylformamide)tetrakis(thiocyanato)cobalt(II)mercury(II), was reported nearly 20 years ago (Kinoshita & Ouchi, 1986). It crystallizes in a non-centrosymmetric space group, but unfortunately the low energy *d*–*d* transitions present in it due to the Co^{2+} ion are normally observed in the visible light region, which limits its SONLO usefulness. Compound (I) is

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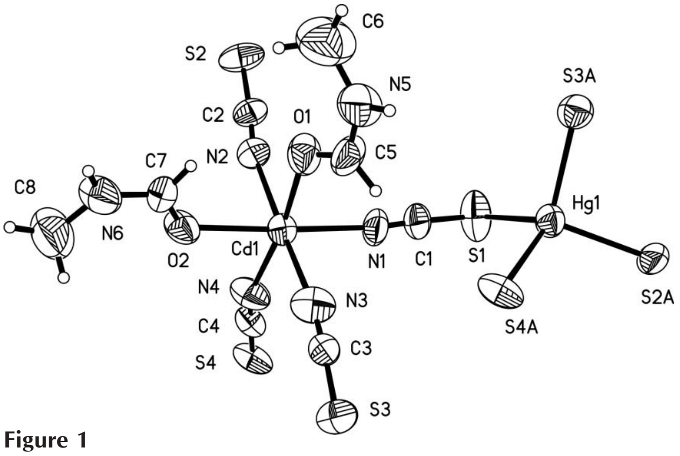

Figure 1
A fragment of the polymeric structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Atoms S2*A*, S3*A* and S4*A* are at the symmetry positions $(x - \frac{1}{2}, \frac{3}{2} - y, z)$, $(1 - x, 2 - y, z + \frac{1}{2})$ and $(x, 1 + y, z)$, respectively.

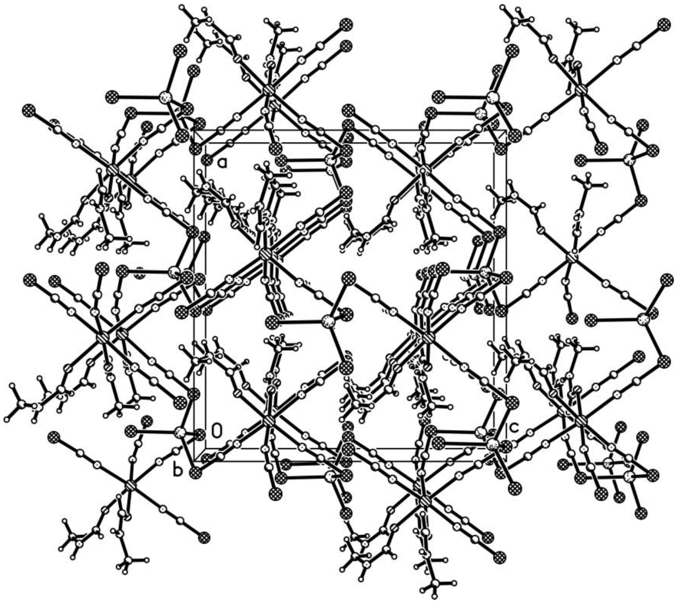

Figure 2
Packing diagram for (I), showing the three-dimensional network.

isostructural with it. However, compound (I) has many better characteristics, such as high SONLO effects and a wide optical transparency range, and it is very easy to grow large high optical quality single crystals.

In the structure of (I) (Fig. 1), each Cd^{II} atom is coordinated by four N atoms belonging to SCN groups and by two O atoms of NMF ligands in a *cis* orientation. The resulting hexacoordinated Cd^{II} centre exhibits slight distortions from ideal octahedral geometry. The Cd1—N2 and Cd1—N3 bond lengths [2.328 (16) and 2.316 (18) Å, respectively] are longer than the Cd1—N1 and Cd1—N4 distances [2.281 (16) and 2.286 (15) Å]. All of them are shorter than the sum of the ionic radii (2.41 Å; Shannon, 1976) and longer than the sum of the single-bond covalent radii (2.23 Å; Pauling, 1960), which indicates that the Cd—N bonds have intermediate covalent and ionic character. The Cd1—O1 and Cd1—O2 bond lengths [2.311 (10) and 2.286 (12) Å, respectively] are close to the sum of the ionic radii (2.30 Å; Shannon, 1976). The values are normal compared with those reported in other similar complexes (Zhou *et al.*, 2000; Guo *et al.*, 2001; Wang *et al.*, 2002). The O1—Cd—O2 bond angle is 87.7 (4)°. The bond angles (between adjacent atoms) O—Cd—N and N—Cd—N are in the ranges 84.4 (4)–94.4 (6) and 89.1 (6)–95.8 (6)°, respectively, and deviate slightly from the ideal octahedral angle of 90°. The other three bond angles, namely O1—Cd1—N4, O2—Cd1—N1 and N2—Cd1—N3, are close to 180° (Table 1).

Each Hg^{II} centre is tetrahedrally coordinated by four S atoms of SCN ligands. The tetrahedra are slightly deformed, with Hg—S bond lengths in the range 2.524 (4)–2.576 (5) Å, averaging 2.540 Å, a little longer than the sum of the single-bond covalent radii (2.52 Å; Pauling, 1960). The S—Hg—S bond angles [range 101.26 (16)–117.8 (2)°] deviate significantly from the ideal tetrahedral angle.

The C—N—Cd angles [range 161.2 (16)–171.5 (16)°] are close to 180°, while the C—S—Hg angles [range 94.1 (5)–98.7 (6)°] are significantly smaller than 180°, exhibiting significant bending. The C—N and C—S bond lengths are slightly shorter than the accepted triple-bond length of 1.16 Å and the normal single bond-length of 1.81 Å, respectively. The SCN groups are quasi-linear, all the N—C—S angles being nearly equal to 180°. The striking feature of these kinds of complexes is that the —S═C═N— bridges, which connect the two metals, form infinite two- or three-dimensional networks; a three-dimensional network is formed in (I) (Fig. 2). The macroscopic non-linear susceptibility of (I) may be related to microscopic hyperpolarizabilities of the dipolar SCN^- ions, and octupolar distorted CdN_4O_2 octahedra and HgS_4 tetrahedra (Zyss & Ledoux, 1994). Such a special infinite three-dimensional network gives a large polarization and can induce a great macroscopic non-linearity. The second harmonic generation (SHG) effect of crystals of (I) was studied by Kurtz & Perry (1968) and found to be nearly the same as that of urea. The optical transmission of a crystal of (I) was measured by a Hitachi U-3500 spectrophotometer and it was found that the UV transparency cutoff is as low as about 360 nm.

Experimental

An NMF solution (15 ml) of CMTC (5.45 g, 10 mmol) was added slowly to water (25 ml) with stirring at room temperature. After a while, compound (I) was precipitated. The crystals used for the X-ray structure analysis were obtained by slow cooling of a solution in NMF and water (2:3, *v*/*v*).

Crystal data

$[CdHg(NCS)_4(C_2H_5NO)_2]$
$M_r = 663.45$
Orthorhombic, $Pna2_1$
$a = 16.244$ (2) Å
$b = 7.7670$ (8) Å
$c = 15.3043$ (19) Å
$V = 1930.9$ (4) Å^3
$Z = 4$
$D_x = 2.282$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 57 reflections
$\theta = 4.8$–$12.5°$
$\mu = 9.49$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.18 × 0.16 × 0.13 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: ψ scan (*XSCANS*; Bruker, 1996)
$T_{\min} = 0.191$, $T_{\max} = 0.290$
2617 measured reflections
2129 independent reflections
1497 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.038$
$\theta_{\max} = 26.0°$
$h = -1 \rightarrow 20$
$k = -9 \rightarrow 1$
$l = -18 \rightarrow 1$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.081$
$S = 0.97$
2129 reflections
201 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0314P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.63$ e Å^{-3}
$\Delta\rho_{\min} = -0.88$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.00277 (15)
Absolute structure: Flack (1983), 151 Friedel pairs
Flack parameter = 0.42 (2)

Table 1
Selected geometric parameters (Å, °).

Hg1—S2$^{\rm i}$	2.524 (4)	N1—C1	1.14 (2)
Hg1—S1	2.528 (5)	N2—C2	1.14 (2)
Hg1—S4$^{\rm ii}$	2.531 (5)	N3—C3	1.13 (2)
Hg1—S3$^{\rm iii}$	2.576 (5)	N4—C4	1.149 (18)
Cd1—N1	2.281 (16)	C2—S2	1.649 (17)
Cd1—O2	2.286 (12)	C3—S3	1.643 (19)
Cd1—N4	2.286 (15)	C4—S4	1.635 (17)
Cd1—O1	2.311 (10)	S3—Hg1$^{\rm iv}$	2.576 (5)
Cd1—N3	2.316 (18)	S4—Hg1$^{\rm v}$	2.531 (5)
Cd1—N2	2.328 (16)	S2—Hg1$^{\rm vi}$	2.524 (4)
S1—C1	1.646 (19)		
S2$^{\rm i}$—Hg1—S1	117.8 (2)	O2—Cd1—N2	84.4 (4)
S2$^{\rm i}$—Hg1—S4$^{\rm ii}$	110.0 (2)	N4—Cd1—N2	89.1 (6)
S1—Hg1—S4$^{\rm ii}$	104.11 (19)	O1—Cd1—N2	87.3 (5)
S2$^{\rm i}$—Hg1—S3$^{\rm iii}$	101.26 (16)	N3—Cd1—N2	174.8 (6)
S1—Hg1—S3$^{\rm iii}$	109.8 (2)	C1—S1—Hg1	95.6 (7)
S4$^{\rm ii}$—Hg1—S3$^{\rm iii}$	114.33 (17)	C1—N1—Cd1	171.5 (16)
N1—Cd1—O2	175.7 (6)	C2—N2—Cd1	165.9 (15)
N1—Cd1—N4	93.3 (6)	C3—N3—Cd1	170.6 (17)
O2—Cd1—N4	85.8 (5)	C4—N4—Cd1	161.2 (16)
N1—Cd1—O1	93.0 (5)	N1—C1—S1	177.5 (18)
O2—Cd1—O1	87.7 (4)	N2—C2—S2	176.1 (18)
N4—Cd1—O1	172.9 (5)	N3—C3—S3	176.5 (16)
N1—Cd1—N3	89.8 (5)	N4—C4—S4	177.7 (18)
O2—Cd1—N3	94.4 (6)	C3—S3—Hg1$^{\rm iv}$	94.1 (5)
N4—Cd1—N3	95.8 (6)	C4—S4—Hg1$^{\rm v}$	98.7 (6)
O1—Cd1—N3	87.6 (5)	C2—S2—Hg1$^{\rm vi}$	95.4 (6)
N1—Cd1—N2	91.4 (6)		

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

H atoms were positioned geometrically (N—H = 0.86 Å and C—H = 0.93 or 0.96 Å) and refined as riding, with $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(carrier atom) for methyl H atoms and $1.2U_{\rm eq}$(carrier atom) for other H atoms. Atoms C6 and C8 of the NMF groups possess large displacement parameters. Since no suitable disorder model was found, their displacements were approximated to isotropic behaviour. Also, restraints were applied to some bond lengths in the NMF groups. The structure is a partial inversion twin, as indicated by the value of the Flack (1983) parameter. The poor precision of the geometric parameters is due to the high thermal motion of some of the atoms at room temperature.

Data collection: *XSCANS* (Bruker, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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