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Cadmium mercury selenocyanate, $CdHg(SeCN)_4$

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Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(N–C) = 0.017 Å
R factor = 0.047
wR factor = 0.119
Data-to-parameter ratio = 27.2

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

$CdHg(SeCN)_4$ has an extended three-dimensional network structure in which the slightly distorted CdN_4 and $HgSe_4$ tetrahedra are connected by –SeCN– bridges.

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Comment

The series of coordination compounds MHg(SCN)$_4$ (where M = Mn, Fe, Co, Ni, Cu, Zn and Cd) have been known for over a century in analytical chemistry for their characteristic structures and colours (Rosenheim, 1901). These complexes have been discovered to be useful second-order nonlinear optical (NLO) materials (Sturmer & Deserno, 1970; Bergman *et al.*, 1970; Yuan *et al.*, 1997; Wang *et al.*, 2001). One of these compounds, $CdHg(SCN)_4$, has been reported to generate second harmonic blue–violet light using GaAlAs laser diodes (Yuan *et al.*, 1997). Since the greater size and polarizability of Se relative to S is expected to induce a larger macroscopic NLO response, as a part of continuing work, we have prepared the title compound, $CdHg(SeCN)_4$, the selenium-substituted analogue of $CdHg(SCN)_4$, and report here its structure and a preliminary investigation of the nonlinear optical behaviour.

The local coordination environments around the metal ions are best described as distorted tetrahedra, CdN_4 and $HgSe_4$.

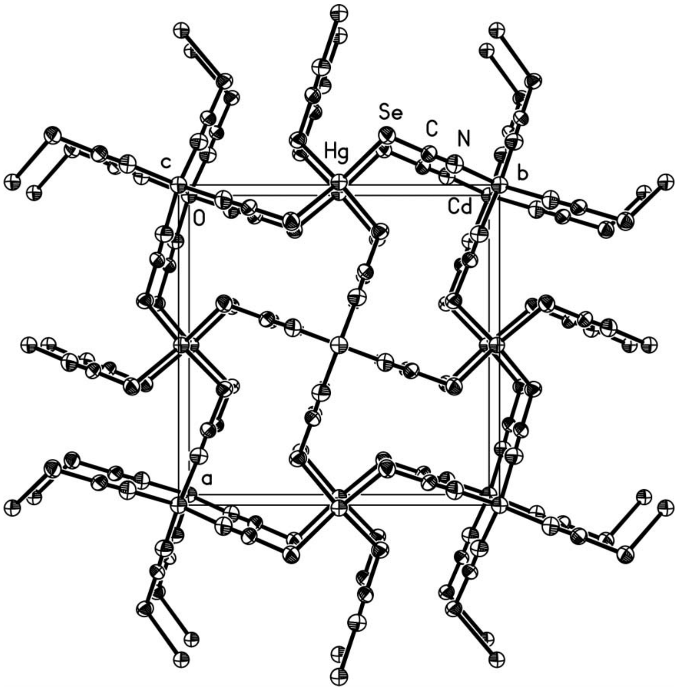

Figure 1
Packing diagram of $CdHg(NCSe)_4$ (viewed down the c axis), with displacement ellipsoids drawn at the 50% probability level.

The bond angles around Cd range from 107.6 (4) to 113.3 (8)°, and those around Hg from 106.92 (3) to 114.69 (6)°. The NCSe ligands are slightly bent, with a bond angle of 177.7 (13)°, and serve as bridges to link adjacent Cd and Hg atoms, thus forming an infinite three-dimensional network (Fig. 1). The macroscopic nonlinear susceptibility may be related to microscopic hyperpolarizabilities of the dipolar SeCN ions and the distorted tetrahedra.

The Hg—Se bond length [2.6666 (12) Å] agrees well with that in $SrHg(SeCN)_4 \cdot 4(pyridine)$ [2.641 (2) Å; Brodersen *et al.*, 1984], both of these values being close to the sum of the atomic radii of Hg and Se (2.61 Å; Pauling, 1960), which shows that the Hg—Se bonds are mostly covalent. A similar situation occurs with the Cd—N bond [2.185 (12) Å], which is very close to the sum of the atomic radii of Cd and N (2.18 Å; Pauling, 1960) but is shorter than that in $CdHg(SCN)_4$ [2.27 (3) Å; Fedorov *et al.*, 1975].

Experimental

$Cd(NO_3)_2 \cdot 4H_2O$, $HgCl_2$ and KSeCN were reacted in a 1:1:4 molar ratio in water. The resulting precipitate was dissolved in a mixed water–acetone solvent (volume ratio 1:4). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of this solution. The second harmonic generation (SHG) effect of the crystals was studied by the Kurtz powder technique (Kurtz & Perry, 1968). It was found that the SHG effect of $CdHg(SeCN)_4$ crystal is over one magnitude greater than that of urea.

Crystal data

$CdHg(SeCN)_4$
$M_r = 732.91$
Tetragonal, $I\bar{4}$
$a = 11.6495$ (6) Å
$c = 4.5128$ (8) Å
$V = 612.44$ (12) Å^3
$Z = 2$
$D_x = 3.974$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 39 reflections
$\theta = 7.4$–17.8°
$\mu = 26.11$ mm^{-1}
$T = 291$ (2) K
Prism, colourless
0.14 × 0.10 × 0.10 mm

Data collection

Bruker *P*4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*XSCANS*; Bruker, 1996)
$T_{\min} = 0.044$, $T_{\max} = 0.073$
1090 measured reflections
896 independent reflections
822 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.029$
$\theta_{\max} = 30.0°$
$h = -16 \rightarrow 16$
$k = -16 \rightarrow 16$
$l = -6 \rightarrow 6$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.119$
$S = 1.09$
896 reflections
33 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0753P)^2 + 2.6748P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 2.20$ e Å^{-3}
$\Delta\rho_{\min} = -1.58$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0103 (12)
Absolute structure: Flack (1983), 394 Friedel pairs
Flack parameter = −0.02 (2)

Table 1
Selected geometric parameters (Å, °).

Hg1—Se1$^{\rm i}$	2.6666 (12)	Se1—C1	1.825 (13)
Cd1—N1	2.185 (12)	N1—C1	1.106 (18)
Se1$^{\rm i}$—Hg1—Se1$^{\rm ii}$	114.69 (6)	C1—Se1—Hg1	95.2 (4)
Se1$^{\rm i}$—Hg1—Se1$^{\rm iii}$	106.92 (3)	C1—N1—Cd1	173.2 (14)
N1—Cd1—N1$^{\rm iv}$	107.6 (4)	N1—C1—Se1	177.7 (13)
N1$^{\rm iv}$—Cd1—N1$^{\rm v}$	113.3 (8)		

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

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

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