Cobalt mercury tetraselenocyanate, CoHg(SeCN)$_4$

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The title compound, CoHg(SeCN)$_4$, was obtained by self-assembly. X-ray crystal structure analysis reveals that it has an extended three-dimensional network structure in which the slightly distorted CoN$_4$ and HgSe$_4$ tetrahedra are connected by –SeCN– bridges. The Hg and Co atoms lie on positions of $\overline{4}$ symmetry.

Comment

Recently, much research interest has been focused on the complexes of the ambidentate thiocyanate (SCN–) and selenocyanate (SeCN–) ligands owing to their striking nonlinear optical (NLO) properties (Zhang *et al.*, 2000; Wang, Xu, Lu, Yuan, Zhang, Meng *et al.*, 2001). The series of coordination compounds MHg(SCN)$_4$ (where M = Mn, Fe, Co, Ni, Cu, Zn and Cd) have been discovered to be useful second-order NLO materials (Sturmer & Deserno, 1970; Bergman *et al.*, 1970; Yuan *et al.*, 1997; Wang, Xu, Lu, Yuan & Xu, 2001). Since the greater size and polarizability of Se relative to S is expected to induce a larger macroscopic NLO response, as a part of our continuing work (Yan *et al.*, 1999; Wang, Xu, Lu, Yuan, Zhang, Xu *et al.*, 2001), we have prepared the title compound, CoHg(SeCN)$_4$ and report here its crystal structure. 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 the CoHg(SeCN)$_4$ crystal is about four times that of urea.

The selenocyanate ion, SeCN$^-$, is a linear triatomic pseudohalide and a highly versatile ambidentate ligand with a polarizable π system. The local coordination environments around the metal ions are best described as distorted tetrahedra, CoN$_4$ and HgSe$_4$. The Hg and Co atoms lie on positions of $\overline{4}$ symmetry. Bond distances and angles have normal values (Orpen *et al.*, 1989). The Se—C—N bond angles are very close to 180° (Fig. 1), *i.e.* the SeCN group is almost linear. The bond angles around Co range from 108.0 (4) to 112.4 (9)°, and those around Hg from 107.78 (3) to 112.91 (6)°. The NCSe ligands are slightly bent, with a bond angle of 178.4 (15)°, and serve as bridges to link adjacent Co and Hg atoms, resulting in the formation of an infinite three-dimensional network (Fig. 1).

The coordination modes in the structure can be rationalized in terms of the hard–soft acid–base concept (Pearson, 1963). The Hg—Se bond length [2.6615 (14) Å] agrees well with that in SrHg(SeCN)$_4$·4(pyridine) [2.641 (2) Å; Brodersen *et al.*, 1984], both of the 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 Co—N bond length [1.967 (13) Å], which is larger than the sum of the atomic radii of Co and N (1.86 Å; Pauling, 1960).
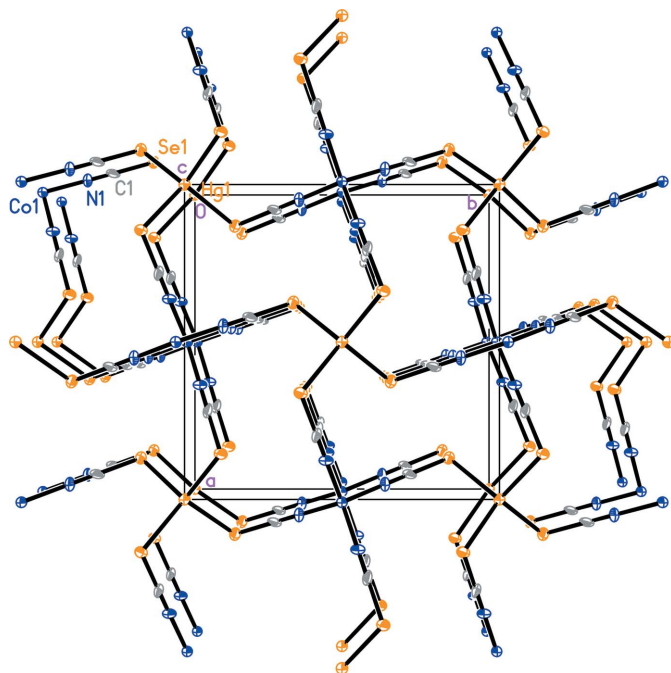
Figure 1
Packing diagram of CoHg(SeCN)$_4$ (viewed down the c axis), with displacement ellipsoids drawn at the 50% probability level.

The C—N [1.13 (2) Å] and C—Se [1.822 (15) Å] bond distances of the selenocyanate ligand suggest electron delocalization upon complex formation. The macroscopic nonlinear susceptibility may be related to microscopic hyperpolarizabilities of the dipolar SeCN$^-$ ions and the distorted tetrahedra. The asymmetric arrangements of Se and N atoms around the metal atom give rise to an asymmetrical metal coordination and a highly asymmetric electron distribution about the metal atom. The extended π-conjugation system within the three-dimensional network structure, with the high polarizabilities of both the metal and the ligand, can induce desirable physical properties such as NLO effects (Zhang *et al.*, 1999). This structure is isomorphous with cadmium mercury selenocyanate, CdHg(SeCN)$_4$ (Sun *et al.*, 2005).

Experimental

Cobalt chloride (2 mmol, 0.260 g) was dissolved in distilled water and then added slowly to a colourless aqueous solution containing mercury chloride (2 mmol, 0.543 g) and potassium selenocyanate (8 mmol, 1.152 g) with stirring. After 1 h the mixture was filtered and the resulting solution was evaporated slowly in a vacuum desiccator. Dark-red block-shaped single crystals were obtained (yield 69.5%, m.p. 500.6 K) after 14 d.

Crystal data

CoHg(SeCN)$_4$	Mo $K\alpha$ radiation
$M_r = 679.44$	Cell parameters from 1547
Tetragonal, $I\bar{4}$	reflections
$a = 11.281$ (3) Å	$\theta = 3.6$–$26.0°$
$c = 4.6207$ (12) Å	$\mu = 26.79$ mm^{-1}
$V = 588.0$ (3) Å^3	$T = 213$ (2) K
$Z = 2$	Block, dark red
$D_x = 3.838$ Mg m^{-3}	$0.40 \times 0.16 \times 0.12$ mm

Data collection

Siemens SMART CCD area-detector diffractometer	566 independent reflections
	545 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.083$
Absorption correction: integration	$\theta_{max} = 26.0°$
($SMART$; Siemens, 1996)	$h = -9 \rightarrow 13$
$T_{min} = 0.009$, $T_{max} = 0.040$	$k = -13 \rightarrow 13$
1547 measured reflections	$l = -5 \rightarrow 5$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$\Delta\rho_{max} = 1.57$ e Å^{-3}
$wR(F^2) = 0.103$	$\Delta\rho_{min} = -1.87$ e Å^{-3}
$S = 1.10$	Extinction correction: $SHELXL97$
566 reflections	Extinction coefficient: 0.0093 (13)
33 parameters	Absolute structure: Flack (1983),
$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2]$	245 Friedel pairs
where $P = (F_o^2 + 2F_c^2)/3$	Flack parameter: 0.06 (3)

Table 1
Selected geometric parameters (Å, °).

Hg1—Se1	2.6615 (14)	Co1—N1	1.967 (13)
Se1—C1	1.822 (15)	N1—C1	1.13 (2)
Co1—N1^i	1.967 (13)		
Se1—Hg1—Se1^{ii}	107.78 (3)	N1^v—Co1—N1	112.4 (9)
Se1—Hg1—Se1^{iii}	112.91 (6)	N1^{vi}—Co1—N1	108.0 (4)
Se1—Hg1—Se1^{iv}	107.78 (3)	C1—N1—Co1	178.4 (15)
C1—Se1—Hg1	95.3 (4)	N1—C1—Se1	178.5 (14)
N1^i—Co1—N1	108.0 (4)		

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

The highest density peak and deepest hole are located 1.61 and 0.75 Å, respectively, from atom Hg1.

Data collection: $SMART$ (Siemens, 1996); cell refinement: $SAINT$ (Siemens, 1996); data reduction: $SAINT$; program(s) used to solve structure: $SHELXTL$ (Sheldrick, 1997); program(s) used to refine structure: $SHELXTL$; molecular graphics: $SHELXTL$; software used to prepare material for publication: $SHELXTL$ and $PLATON$ (Spek, 2003).

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