Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Manganese mercury selenocyanate, $MnHg(SeCN)_4$

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(N–C) = 0.016 Å
R factor = 0.052
wR factor = 0.134
Data-to-parameter ratio = 38.8

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

Received 23 November 2006
Accepted 14 January 2007

$MnHg(SeCN)_4$ has a three-dimensional network in which slightly distorted MnN_4 and $HgSe_4$ tetrahedra (symmetry $\overline{4}$) are connected by –SeCN– bridges.

Comment

Tetra(thiocyanato)mercurates of transition metal ions such as Mn, Fe, Co, Zn and Cd crystallize in non-centrosymmetric structures, most exhibiting excellent second-order nonlinear optical (NLO) effects. Among these, $MnHg(SCN)_4$ exhibits powder second harmonic generation (SHG) efficiency 50 times greater than that of urea and shows good transparency in the UV region (Yan *et al.*, 1999; Wang *et al.*, 2002).

Like SCN^-, $SeCN^-$ is a linear triatomic pseudohalide and a versatile ambidentate ligand with a polarizable π system. Because of the decreased electronegativity of the Se atom, the π-bonds will be essentially localized between the C and N atoms. Coordination to the soft Hg^{II} centres by $SeCN^-$ ligands through the softer Se atoms may provide more highly ordered networks than by SCN^- ligands. This may induce a larger macroscopic NLO response. The structure and NLO behaviour of $MnHg(SeCN)_4$ are reported here.

The three-dimensional network consists of slightly distorted MnN_4 [107.6 (5) and 113.2 (10)°] and $HgSe_4$ tetrahedra [107.35 (2) and 113.80 (5)°], linked together by the bridging $SeCN^-$ ions, which bind with hard Mn^{II} ions through the N atom, and with soft Hg^{II} ions through the Se atom. The C—N—Mn group is nearly linear and the C—Se—Hg group is bent. The Se—C—N group is essentially linear, with C—N distances slightly shorter than a triple bond (1.16 Å) and C—Se distances considerably shorter than a single bond (1.94 Å), consistent with other $SeCN^-$ complexes (Swank & Willett, 1965; Brodersen *et al.*, 1984; Wells, 1991; Sun *et al.*, 2005, 2006; Li *et al.*, 2006).

The macroscopic nonlinear susceptibility of $MnHg(SeCN)_4$ crystals may be related to microscopic hyperpolarizabilities of the dipolar $SeCN^-$ ions and octupolar distorted MnN_4 and $HgSe_4$ tetrahedra (Zyss & Ledoux, 1994). The SHG efficiency of $MnHg(SeCN)_4$ crystal powder has been measured by the Kurtz & Perry (1968) technique and found to be about nine times higher than that of polycrystalline urea powder.

$MnHg(SeCN)_4$ is isomorphous with the previously reported compounds $CdHg(SeCN)_4$ (Sun *et al.*, 2005), $CoHg(SeCN)_4$ (Li *et al.*, 2006) and $ZnCd(SeCN)_4$ (Sun *et al.*, 2006). Magnetic susceptibility measurements at room temperature indicate that $MnHg(SeCN)_4$ is paramagnetic.

Experimental

Manganese(II) chloride tetrahydrate (1 mmol, 0.198 g) was dissolved in distilled water and then added slowly to an aqueous solution containing mercury(II) chloride (1 mmol, 0.272 g) and potassium selenocyanate (4 mmol, 0.576 g) with stirring. After several minutes, the mixture was filtered and the resulting colourless solution was evaporated slowly in a vacuum desiccator. Colourless, transparent, prism-shaped crystals of $\mathrm{MnHg(SeCN)_4}$ were formed after 2 d. IR (Nicolet 750 FTIR spectrometer, $\mathrm{cm^{-1}}$): 2130 and 2080 [ν(CN)], 827 and 800 [2δ(SeCN)], 618 [ν(CSe)], 414 and 402 [δ(SeCN)]. From thermal analysis, $\mathrm{MnHg(SeCN)_4}$ was found to be stable up to 554 K.

Crystal data

$\mathrm{MnHg(SeCN)_4}$
$M_r = 675.45$
Tetragonal, $I\bar{4}$
$a = 11.4545$ (4) Å
$c = 4.5803$ (4) Å
$V = 600.96$ (6) Å^3
$Z = 2$

$D_x = 3.733$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 25.89$ mm^{-1}
$T = 295$ (2) K
Prism, colourless
0.15 × 0.11 × 0.09 mm

Data collection

Bruker APEX2 CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*APEX2*; Bruker, 2005)
$T_{\min} = 0.032$, $T_{\max} = 0.096$

2040 measured reflections
1282 independent reflections
1030 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.058$
$\theta_{\max} = 35.8°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.134$
$S = 0.98$
1282 reflections
33 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0617P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 2.37$ e Å^{-3}
$\Delta\rho_{\min} = -4.40$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0045 (11)
Absolute structure: Flack (1983), 528 Friedel pairs
Flack parameter: 0.03 (2)

Table 1
Selected bond lengths (Å).

Hg—Se	2.6595 (10)	Mn—N^{i}	2.060 (13)
Se—C	1.795 (12)	N—C^{ii}	1.152 (17)

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

The highest peak and deepest hole in the final difference Fourier map lie 1.00 and 0.70 Å, respectively, from the Hg atom.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

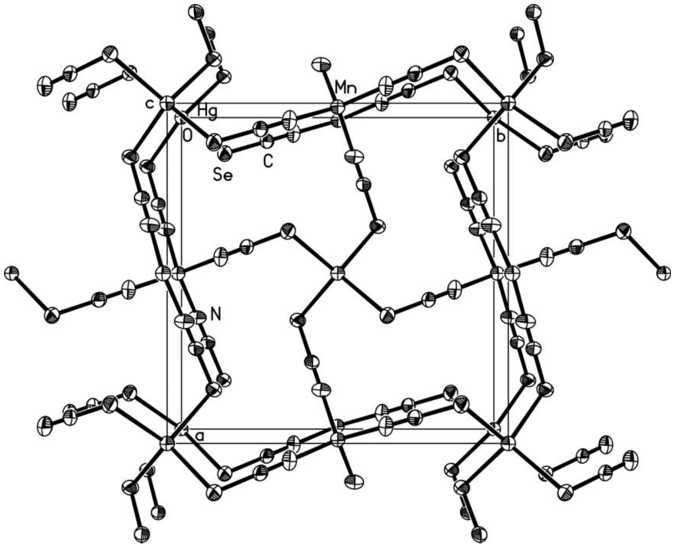

Figure 1
$\mathrm{MnHg(SeCN)_4}$ (viewed down the *c* axis) with displacement ellipsoids drawn at the 50% probability level.

This work was supported by the Foundation for the Authors of National Excellent Doctoral Dissertations of the People's Republic of China (No. 200539) and grants (Nos. 60476020, 60608010, 50672049, 60377016 and 50323006) from the National Natural Science Foundation of China.

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