Polymeric $Cd(Se\text{-}2\text{-}NC_5H_4)_2$ and Square Planar $Hg(Se\text{-}2\text{-}NC_5H_4)_2$: Volatile CVD Precursors to II–VI Semiconductors

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Pyridineselenolate complexes of Cd(II) and Hg(II) have been prepared by proton transfer reactions of pyridineselenol with metal carboxylates. The compounds have been characterized by NMR and IR spectroscopy and by single-crystal X-ray diffraction. The cadmium complex crystallizes in the monoclinic space group $C2/c$, with $a = 30.163(5)$ Å, $b = 7.574(1)$ Å, $c = 20.862(2)$ Å, $\beta = 96.20(1)°$, $V = 4738(1)$ Å, $Z = 4$, and $\rho_{calc} = 2.392$ g/cm^3 (Mo Kα radiation at 23 °C). The crystal structure is that of a one-dimensional array of cadmium ions and two bridging pyridineselenolate ligands, with both selenium atoms and one nitrogen atom of each ligand pair binding to each metal. The mercury complex crystallizes in the space group $P2_1/n$ with $a = 11.208(1)$ Å, $b = 4.169(1)$ Å, $c = 12.706(1)$ Å, $\beta = 100.55(1)°$, $V = 583.7(2)$ Å, $Z = 2$, and $\rho_{calc} = 2.929$ g/cm^3 (Mo Kα radiation at 23 °C). The square planar mercury ions are bound to a pair of chelating pyridineselenolate ligands, with weak contacts between the mercury ion and two selenium atoms from adjacent molecules. Both compounds sublime without decomposition and decompose at higher temperatures to give solid-state MSe.

Introduction

Considerable effort has been directed toward the synthesis of molecules which decompose in a controlled fashion to give II–VI semiconductor materials, and the majority of work has focused on the preparation of metal chalcogenolates $M(ER)_2$ (M = Zn, Cd, Hg; E = S, Se, Te).[1] The thermal decomposition of these group 10 metal chalcogenolates to give binary ME materials has long been recognized, and while these molecules would seem likely candidates for chemical vapor deposition (CVD) processes, they are generally involatile polymeric compounds.

There a number of possible synthetic approaches to enhancing compound volatility. The suppression of polymer formation with the use of sterically demanding chalcogenolate ligands has been recently reported,[2] but these sterically saturated compounds show an increased tendency to reductively eliminate dichalcogenide and give elemental metal, rather than metal chalcogenide. An alternative route to volatile precursors involves saturating the metal coordination sphere with strong neutral donor ligands,[1d,e] but such ligands do not necessarily enhance compound volatility because they tend to dissociate at temperatures lower than the temperatures at which the neutral complex sublimes, and this ligand dissociation process diminishes the utility of the precursor in CVD processes.

There are two ways the chelate effect can be used to minimize neutral ligand dissociation. First, neutral bidentate ligands can be used to prepare molecular species, and the enhanced stability of the bidentate linkage should enhance complex stability. Second, the chalcogenolate ligand can be derivatized by covalently linking the neutral donor to chalcogenolate functionality.[3] This approach ensures neutral donor proximity as long as the chalcogenolate ligand is bound to the metal center.

In this paper, we describe the use of the pyridineselenolate ligand to prepare stable metal chalcogenolates, and we report the synthesis and structural characterization of $Cd(Se\text{-}2\text{-}NC_5H_4)_2$ (**1**) and $Hg(Se\text{-}2\text{-}NC_5H_4)_2$ (**2**). The cadmium compound is polymeric in the solid state, and the mercury derivative can be described as square planar, with weak interactions between the mercury ion of one complex and two selenium atoms from the two neighboring molecules along the crystallographic *b*-axis. Both molecules sublime without decomposition at relatively low temperatures and decompose at higher temperatures to give microcrystalline solid-state metal selenide.

Experimental Section

General Methods. All syntheses were carried out under ultrapure nitrogen (JWS), using conventional drybox or Schlenk techniques. Solvents were refluxed continuously over molten alkali metals or sodium/benzophenone and collected immediately prior to use. Melting points were taken in sealed capillaries and are uncorrected. Powder diffraction spectra were obtained from a SCINTAG PAD V diffraction meter and monochromatized Cu Kα radiation. GCMS data were collected from a 5890 Series II gas chromatograph with an HP 5971 mass selective detector. IR spectra were taken by diffuse reflectance in KBr using a Perkin-Elmer 1720× FTIR at 4-cm^{-1} resolution from 4000 to 450 cm^{-1}. NMR spectra were recorded on a Varian XL 200 MHz NMR at 24.5 °C. Elemental analyses were preformed by Quantitative Technologies, Inc. (Salem, NJ).

Synthesis of $HSeNC_5H_4$. The reported syntheses of pyridine-2-selenol[4] were unreliable in our hands, and so we explored variations of the published procedures. NaHSe[5] was prepared by adding sodium borohydride (2.1 g, 55.5 mmol) to a solution of selenium (4.0 g, 50.7 mmol) in a mixture of anhydrous ethanol and anhydrous chloroform (75 mL:25 mL) at 0 °C under nitrogen. After 30 min the solution was brought to room temperature, and after an additional 30 min, the colorless solution was taken to dryness under vacuum to give a white powder (NaHSe). Ammonium chloride (0.5 g, 9.3 mmol), 2-bromopyridine (4.83 mL, 8.0 g, 50.7 mmol), and anhydrous dimethylformamide (100 mL) were added,

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and the mixture was heated to 85 °C in the dark for 15 h. The solvent was removed under vacuum, and the yellow powder was washed first with cool water (100 mL) and then with a cool mixture of hexane and methanol (150 mL:50 mL). The solid was dissolved in CH_2Cl_2 (75 mL), and the solution was filtered and cooled (−20 °C) to give yellow crystals of pyridine-2-selenol (4.5 g, 56%) that was identified by mp (132 °C) and ^1H NMR ($CDCl_3$): 8.41 (1H, broad), 7.86 (1H, d), 7.71 (1H, d), 7.38 (1H, t) and 6.98 (1H, t).

Synthesis of Cd(Se-2-NC_5H_4)$_2$. Pyridine-2-selenol (2.5 g, 15.9 mmol) was dissolved in methanol (100 mL) with vigorous stirring. Cadmium bis(2-ethylhexanoate) (3.15 g, 7.96 mmol) was added to the yellow solution to give a white precipitate. The precipitate was collected by filtration and washed by methanol (100 mL) to give a white solid (3.25 g, 90%). X-ray-quality crystals were isolated by dissolving a portion of the white solid (1.00 g) in pyridine at 100 °C; a bubbler was connected to the apparatus, and over 4 days colorless needlelike crystals formed along the edge of the evaporating pyridine solution (0.20 g, 20%, mp 210–215 °C dec). Anal. Calcd for $CdC_{10}H_8N_2Se_2$: C, 28.2; H, 1.89; N, 6.57. Found: C, 28.6; H, 2.20; N, 6.31. IR: 1578 (s), 1547 (s), 1470 (w), 1443(s), 1414 (s), 1265 (m), 1231 (w), 1151 (m), 1115 (s) 1079 (m), 1041 (m), 1003 (m), 765 (m), 750 (s), 698 (m), 637 (m) and 473 (m) cm^{-1}. ^1H NMR (DMSO): 7.80 (1H, d), 7.47 (1H, d), 7.34 (1H, t), and 6.93 (1H, t). The compound sublimes without decomposing (185 °C, 0.1 mmHg).

Synthesis of Hg(Se-2-NC_5H_4)$_2$. Pyridine-2-selenol (2.0 g, 12.7 mmol) was dissolved in CH_2Cl_2 (100 mL), and Hg(acetate)$_2$ (2.07 g, 6.37 mmol) was added to the solution under vigorous stirring in the dark.[6] After 10 min, the solution was colorless. The solution was filtered, concentrated to ca. 50 mL, and cooled (0 °C) to give colorless needlelike crystals; second, third, and fourth crops were isolated in identical fashion and combined to give Hg($SeNC_5H_4$)$_2$ (3.07 g, 92%; mp 141.7 °C (dec 185 °C)). Anal. Calcd for $HgC_{10}H_8N_2Se_2$: C, 23.3; H, 1.57; N, 5.44. Found: C, 23.3; H, 1.55; N, 5.35. IR: 1570 (s), 1551 (s), 1444 (s), 1409 (s), 1275 (m), 1149 (m), 1109 (s), 1080 (s), 1042 (m), 983 (m), 958 (w), 879 (w), 744 (s), 694 (s), 618 (w), 467 (m) cm^{-1}. ^1H NMR ($CDCl_3$): 8.12 (d, 1H), 7.40 (m, 2H), 7.01 (d, 1H). The compound sublimes without decomposition (110 °C, 0.1 mmHg).

Thermolysis of 1 and 2. **1** (0.5 g, 1.17 mmol) was sealed in an evacuated Pyrex tube. After **1** was heated overnight at 270 °C, red microcrystalline CdSe (0.21g, 93%) was collected and identified by X-ray powder diffraction.[7] The volatile products were collected at the cool end of the tube and identified by GCMS as 2,2′-selenodipyridine (M^+, *m/e* 234).[8]

In Solution. **1** (0.10 g, 0.23 mmol) was dissolved in DMSO (30 mL). The colorless solution was refluxed at 192 °C for 14 h to give a yellow-green solution and a red precipitate. After 8 days, the red precipitate was collected and identified as CdSe (40 mg, 89%) by X-ray powder diffraction. The GC mass spectrum of the solution phase indicates traces of 2-methylpyridine (M^+, *m/e* 93), 2-ethylpyridine (M^+, *m/e* 107), and a major fraction due to Py-2-SeS(=O)CH_3 (M^+, *m/e* 219). The compound was stable in refluxing DMF. There was no evidence for the formation of 2,2′-selenodipyridine.

2 (0.50 g, 0.97 mmol) was sealed in an evacuated Pyrex tube and heated at 250 °C overnight to give black microcrystalline HgSe (0.26 g, 96%), which was identified by powder X-ray diffraction.[8] The volatile product was collected at the cool end of the tube and identified as 2,2′-selenodipyridine by GCMS (M^+, *m/e* 234).

In Solution. **2** (0.50 g, 0.97 mmol) was dissolved in *N,N*-dimethylformamide (50 mL) to give a light yellow solution. The solution was heated at 110 °C overnight, the color turned deep yellow-green, and a black powder precipitated. After 7 days, the black powder was collected (0.23 g, 86%) and X-ray powder diffraction indicated the formation of HgSe as the only crystalline product. GCMS of the residual solution indicated the presence of both 2,2′-selenodipyridine (M^+, *m/e* 234) and 2,2′-diselenodipyridine (M^+, *m/e* 312).

X-Ray Crystallography of 1 and 2. Single-crystal X-ray diffraction data for rod-shaped crystals of **1** and **2** were collected in the ω–θ scan mode on a CAD4 diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). The data were corrected for Lorenz effects and polarization. The absorption corrections for **1** (0.03 × 0.09 × 0.35 mm) and **2** (0.06 × 0.08 × 0.30 mm) were based on a Gaussian grid method (SHELX76).[9] Three check reflections were measured every 3 h and showed negligible intensity loss for both crystals, although by the end of data collection both crystals had turned slightly yellow. Both structures were solved by Patterson methods (SHELXS86).[10] All non-hydrogen atoms were refined using full-matrix least squares based upon F_o^2 (SHELXL93)[11] with anisotropic thermal parameters. The isotropic extinction coefficient for **2** (0.0132) and scattering factors (f_o, $f\,'$, $f\,''$) are as described in SHELXL93.[11] All hydrogen atom coordinates were calculated with bond distances of 0.95 Å. Crystallographic data and final *R* indicies are given in Table 1.

Table 1. Crystal Data and Structure Refinement for {Cd(Se-2-NC_5H_4)$_2$}$_n$ and Hg(Se-2-NC_5H_4)$_2$

empirical formula	$C_{20}H_{16}Cd_2N_4Se_4$	$C_{10}H_8HgN_2Se_2$
fw	853.01	514.69
space group	*C*2/*c* (No. 15)	*P*2$_1$/*n* (No. 14)
a (Å)	30.163(5)	11.208(1)
b (Å)	7.574(1)	4.169(1)
c (Å)	20.862(2)	12.706(1)
β (deg)	96.20(1)	100.55(1)
V (Å^3)	4738(1)	583.7(2)
Z	8	2
D (calcd) (Mg/m^3)	2.392	2.929
T (K)	293(2)	293(2)
λ (Å)	0.710 73	0.710 73
abs coef. (mm^{-1})	7.96	19.4
$R(F_o)^a$ (all data)	0.180	0.056
$R_w(F_o^2)^a$ (all data)	0.222	0.087

[a] Definitions: $R(F_o) = \sum||F_o| - |F_c|| / \sum|F_o|$. $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$.

Discussion

The pyridineselenolate ligand forms stable, volatile complexes with Cd and Hg. The cadmium complex is best prepared by the proton transfer reaction between pyridine-2-selenol and cadmium ethylhexanoate in ethanol. The final product is insoluble in ethanol and can be recrystallized from hot pyridine. The mercury complex can be prepared similarly. The mercury pyridineselenolate complex is more soluble than the Cd compound and can be crystallized from chloroform or donor solvents.

Both complexes sublime without decomposition. The mercury derivative is considerably more volatile, sublimes readily at 110 °C (ca. 10^{-2} Torr), melts at 142 °C, and decomposes cleanly at 183 °C to give HgSe. The cadmium complex does not melt but sublimes at 185 °C and decomposes slowly at 210–215 °C to give CdSe. The relatively low sublimation temperatures and higher decomposition points make these compounds potentially valuable CVD precursors. The isolated compounds can be converted thermally into solid state metal selenide. Analysis of the volatile products of these thermolysis reactions reveals only the presence of dipyridine monoselenide. In solution, both molecules are converted to microcrystalline MSe at significantly lower temperatures and thus are potential precursors to nanoscale semiconductor clusters,[1d] but an analysis of the organic products indicates that more complicated reaction pathways are also accessible. When dissolved in refluxing DMF, **1** does not decompose, and **2** decomposes to give a mixture of dipyridine monoselenide and dipyridine diselenide. In refluxing DMSO, **1** gives CdSe, but the large number of organic products indicates that radical formation may be an important decomposition mechanism.

From the distinctly different melting and sublimation temperatures of the two compounds, we presumed that they were structurally unrelated. This was confirmed when both compounds were subjected to single crystal X-ray diffraction experiments. Table 1 gives a listing of crystallographic details for both

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Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for {[Cd(Se-2-NC$_5$H$_4$)$_2$]$_2$}$_n$[a]

	x	*y*	*z*	*U*(eq)
Cd(1)	3675(1)	7963(2)	1448(1)	34(1)
Cd(2)	3856(1)	13174(2)	1066(1)	35(1)
Se(1)	4003(1)	5164(2)	2225(1)	41(1)
Se(2)	3552(1)	6005(2)	293(1)	39(1)
Se(3)	4412(1)	9815(2)	1291(1)	40(1)
Se(4)	3118(1)	11401(2)	1231(1)	43(1)
N(1)	4578(5)	4531(19)	1309(7)	37(4)
N(2)	2935(5)	6711(19)	1148(7)	38(4)
N(3)	4060(5)	11553(18)	196(7)	38(4)
N(4)	3429(5)	9515(18)	2322(7)	38(4)
C(1)	4564(6)	5246(22)	1889(10)	55(6)
C(2)	4942(7)	6049(26)	2210(11)	56(6)
C(3)	5326(7)	5955(29)	1953(14)	71(8)
C(4)	5347(7)	5195(28)	1344(14)	71(7)
C(5)	4956(6)	4543(27)	1066(11)	58(6)
C(6)	2969(5)	5933(22)	586(8)	32(4)
C(7)	2605(7)	5252(28)	216(11)	61(6)
C(8)	2208(7)	5281(27)	460(9)	50(5)
C(9)	2166(7)	6019(26)	1049(13)	64(7)
C(10)	2559(8)	6732(26)	1342(11)	65(6)
C(11)	4301(5)	10118(22)	377(8)	32(4)
C(12)	4439(7)	8911(25)	−63(11)	56(6)
C(13)	4364(7)	9290(28)	−687(11)	61(6)
C(14)	4108(8)	10729(30)	−909(9)	65(7)
C(15)	3969(7)	11793(24)	−439(10)	50(5)
C(16)	3224(6)	10987(22)	2136(9)	37(4)
C(17)	3066(6)	12052(26)	2567(11)	52(5)
C(18)	3103(6)	11638(29)	3220(12)	60(6)
C(19)	3313(7)	10123(30)	3401(10)	62(6)
C(20)	3471(6)	9074(22)	2954(8)	36(4)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized **U**$_{ij}$ tensor.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for Hg(SeNC$_5$H$_4$)[a]

	x	*y*	*z*	*U*(eq)
Hg	5000	0	0	40(1)
Se	6528(1)	3343(2)	−639(1)	40(1)
C(1)	5476(5)	4407(14)	−1947(4)	32(1)
N(2)	4336(5)	3412(19)	−2089(4)	44(1)
C(3)	3604(7)	4289(23)	−3016(6)	54(2)
C(4)	3991(7)	6037(24)	−3793(6)	55(2)
C(5)	5166(8)	7029(23)	−3634(6)	54(2)
C(6)	5945(6)	6177(22)	−2700(5)	44(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized **U**$_{ij}$ tensor.

compounds. Tables 2 and 3 give listings of atomic positions for **1** and **2**, respectively.

The cadmium complex crystallizes as a one-dimensional polymer (Figure 1), and is similar to, although not isostructural with, the analogous thiopyridine complex Cd(S-2-NC$_5$H$_4$)$_2$.[12] Significant bond distances and angles for **1** are given in Table 4. In the crystal structure there are two unique metal ions with nearly identical coordination environments; each metal center coordinates four selenium and two nitrogens in a distorted octahedral geometry, and each metal ion is connected to two adjacent metal ions through a pair of bridging selenium atoms. The two nitrogen donors associated with each pair of pyridineselenolate bridges bind one each to the metal ions before and after the selenium pair. Within the structure, there are no bond geometries that would be indicative of any selenoketone–metal amido resonance structure contribution to complex stability. The metal–ligand bond lengths are consistent with previously reported values.

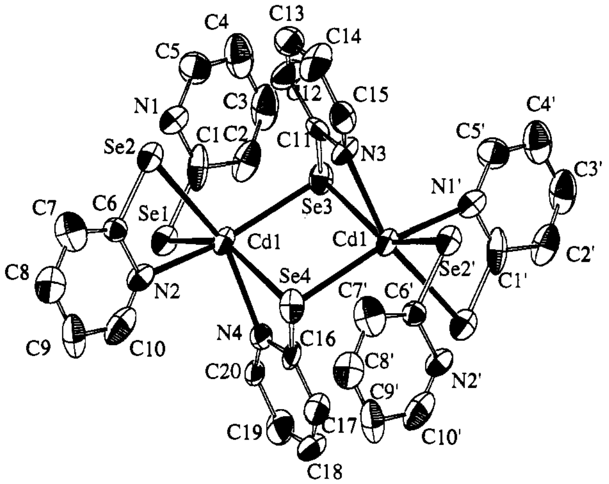

Figure 1. Molecular structure of polymeric Cd(Se-2-NC$_5$H$_4$)$_2$. There are two nearly identical Cd atoms, rotated by about 90° with respect to one another along the polymer axis. The 6-coordinate Cd atoms (4 Se, 2 N) are arranged in an extended array of propagating Cd$_2$Se$_2$ squares at right angles to adjacent Cd$_2$Se$_2$ units. One pyridine ring extends above each square and one extends below, with the N atoms making contact to opposite Cd atoms. Average bond lengths (Å): Cd–Se, 2.85 (range 2.68–3.11); Cd–N, 2.40(2).

Table 4. Bond lengths (Å) and Angles (deg) for {[Cd(Se-2-NC$_5$H$_4$)$_2$]$_2$}$_n$[a]

Cd(1)–N(4)	2.36(1)	Cd(1)–N(2)	2.44(1)
Cd(1)–Se(3)	2.677(2)	Cd(1)–Se(1)	2.785(2)
Cd(1)–Se(2)	2.820(2)	Cd(1)–Se(4)	3.106(2)
Cd(2)–N(3)	2.33(1)	Cd(2)–N(1)′	2.41(1)
Cd(2)–Se(4)	2.655(2)	Cd(2)–Se(2)′	2.779(2)
Cd(2)–Se(1)′	2.843(2)	Cd(2)–Se(3)	3.055(2)
Se(1)–C(1)	1.90(2)	Se(1)–Cd(2)″	2.843(2)
Se(2)–C(6)	1.92(2)	Se(2)–Cd(2)″	2.779(2)
Se(3)–C(11)	1.91(2)	Se(4)–C(16)	1.91(2)

N(4)–Cd(1)–N(2)	92.1(5)	N(4)–Cd(1)–Se(3)	99.7(3)
N(2)–Cd(1)–Se(3)	156.8(4)	N(4)–Cd(1)–Se(1)	92.9(4)
N(2)–Cd(1)–Se(1)	96.3(3)	Se(3)–Cd(1)–Se(1)	102.87(7)
N(4)–Cd(1)–Se(2)	154.2(3)	N(2)–Cd(1)–Se(2)	62.9(4)
Se(3)–Cd(1)–Se(2)	101.86(7)	Se(1)–Cd(1)–Se(2)	95.90(6)
N(4)–Cd(1)–Se(4)	58.9(4)	N(2)–Cd(1)–Se(4)	79.8(3)
Se(3)–Cd(1)–Se(4)	89.23(6)	Se(1)–Cd(1)–Se(4)	151.13(8)
Se(2)–Cd(1)–Se(4)	107.27(6)	N(3)–Cd(2)–N(1)′	94.6(5)
N(3)–Cd(2)–Se(4)	97.4(4)	N(1)′–Cd(2)–Se(4)	160.0(4)
N(3)–Cd(2)–Se(2)′	93.0(3)	N(1)′–Cd(2)–Se(2)′	91.6(3)
Se(4)–Cd(2)–Se(2)′	103.67(7)	N(3)–Cd(2)–Se(1)′	155.9(3)
N(1)′–Cd(2)–Se(1)′	62.7(4)	Se(4)–Cd(2)–Se(1)′	102.40(7)
Se(2)′–Cd(2)–Se(1)′	95.52(6)	N(3)–Cd(2)–Se(3)	59.6(3)
N(1)′–Cd(2)–Se(3)	81.6(3)	Se(4)–Cd(2)–Se(3)	90.76(7)
Se(2)′–Cd(2)–Se(3)	150.77(8)	Se(1)′–Cd(2)–Se(3)	106.19(6)
C(1)–Se(1)–Cd(1)	92.0(5)	C(1)–Se(1)–Cd(2)″	76.5(6)
Cd(1)–Se(1)–Cd(2)″	84.01(6)	C(6)–Se(2)–Cd(2)″	92.8(5)
C(6)–Se(2)–Cd(1)	77.5(5)	Cd(2)″–Se(2)–Cd(1)	84.54(6)
C(11)–Se(3)–Cd(1)	97.3(4)	C(11)–Se(3)–Cd(2)	73.4(5)
Cd(1)–Se(3)–Cd(2)	90.34(7)	C(16)–Se(4)–Cd(2)	99.1(5)
C(16)–Se(4)–Cd(1)	71.8(5)	Cd(2)–Se(4)–Cd(1)	89.67(1)

[a] Symmetry transformations used to generate equivalent atoms: (′) *x*, *y* + 1, *z*; (″) *x*, *y* − 1, *z*.

The molecular structure of **2** contains a *trans* MA$_2$B$_2$ square planar mercury ion (Figure 2). Table 5 gives a listing of important distances and angles within the molecule. The Hg ion resides on an inversion center, giving one unique Hg–Se and one unique Hg–N bond and Se–Hg–Se and N–Hg–N angles of 180°. The Hg–Se bond length of 2.46 Å is similar to previously reported Hg–Se bond lengths,[13,14] while the Hg–N bond length of 2.98 Å in **2** is considerably longer than the mercury–nitrogen bond lengths found in the related tetrameric[14] structures of HgCl(py)(SeEt) (Hg–N = 2.45 Å) or HgCl(py)$_{0.5}$(SeBu^t) (Hg–N = 2.49 Å). This extremely long bond likely indicates that the metal–pyridine interaction is very weak. There are two additional close contacts between the mercury ion and selenium atoms from neighboring

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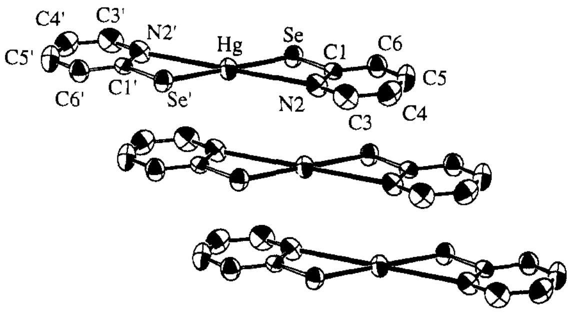

Figure 2. Molecular structure of Hg(Se-2-NC_5H_4)$_2$. The complex is approximately planar, with no atom deviating more than 0.05 Å. There are close "nonbonded contacts" between the mercury atom and two selenium atoms from the adjacent molecules along the crystallographic *b*-axis shown here. Significant bond lengths (Å): Hg–Se, 2.4581(7); Hg–N, 2.984(1). Significant bond angles (deg): Se–Hg–Se', 180; Se–Hg–N, 60.7(1).

Table 5. Bond Lengths (Å) and Angles (deg) for Hg($SeNC_5H_4$)$_2$[a]

	Bond Lengths		
Hg–Se	2.458(1)	Hg–N(2)	2.984(1)
Se–C(1)	1.905(6)	C(1)–N(2)	1.324(8)
C(1)–C(6)	1.386(9)	N(2)–C(3)	1.356(9)
C(3)–C(4)	1.36(1)	C(4)–C(5)	1.36(1)
C(5)–C(6)	1.38(1)		
	Bond Angles		
Se'–Hg–Se	180.0	Se–Hg–N(2)	60.7(1)
C(1)–Se–Hg	93.6(2)	N(2)–C(1)–C(6)	123.4(6)
N(2)–C(1)–Se	118.3(4)	C(6)–C(1)–Se	118.3(5)
C(1)–N(2)–C(3)	116.7(6)	N(2)–C(3)–C(4)	123.5(7)
C(5)–C(4)–C(3)	118.9(7)	C(4)–C(5)–C(6)	119.4(7)
C(1)–C(6)–C(5)	117.9(7)		
	Nonbonded Contacts (along the *b* Axis)		
Hg···Se''	3.435(1)	Hg···N(2)'	3.798(1)
Hg···C(1)'	3.510(1)		

[a] Symmetry transformations used to generate equivalent atoms: (') $-x + 1, -y, -z$; ('') $x, y - 1, z$.

square planar units which resemble, in terms of relative bond lengths, the interactions between the linear mercury halides and neighboring halide ions in the crystal structures of HgX_2, X = Cl, Br.[15]

The analogous mercury thiopyridine structure also contains mercury(II) ions in a square planar environment, but the mercury coordination sphere contains only bridging sulfur atoms, and the pyridine nitrogen atoms remain uncoordinated.[6] In **2**, the relatively weaker Hg–Se bonds are displaced by the nitrogen donors, while the the linear arrangement of chalcogen ligands bound to the Hg is maintained. This linearity is common in mercury dithiolate systems (R = SMe,[16] SEt,[17] S-2-py[6]), but for mercury selenolates both linear structures (R = SeMe,[16] Se-2,4,6-tri-Pr^i-C_6H_2[2], Se-2,4,6-tri-Bu^t-C_6H_2[2]) and coordination polymers (R = Se-t-Bu,[13] Se-2,4,6 tri-Bu^t-C_6H_2[2]) have been observed. The structures of the three trisubstituted areneselenolates of mercury illustrate the apparent ease with which the metal rehybridizes to accommodate the steric requirements of the organic ligands.

The relatively low sublimation temperature of this mercury selenide precursor can be understood in the context of the solid-state structure . Because the complex is molecular, there are no covalent bonds to be broken before the compound can vaporize. Further, the complete absence of a dipole moment in the complex serves to minimize electrostatic interactions between square planar units in the solid state, and this may also serve to minimize the energy necessary to vaporize the compound. Hence the mercury derivative is more volatile than the analogous Cd derivative, where the compound is polar and the metal ions are connected through a network of covalent bonds.

Conclusion

The pyridineselenolate ligand can be used to prepare stable complexes of Cd and Hg, and these compounds decompose cleanly to give solid-state metal selenide. Both compounds are volatile at temperatures well below their decomposition temperatures, and thus are excellent candidates for CVD processes. The bifunctionality of this ligand, coupled with its relatively small bite angle, leads to a rich structural chemistry. The distorted octahedral geometry of the cadmium compound differs significantly from previously reported CdSe precursor compounds which were typically in a tetrahedral geometry. The square planar mercury coordination sphere is also unusual and can be interpreted in terms of a linear array of two strong Hg–Se bonds within the molecule, weak interactions between the Hg atom and the nitrogen donors within the molecule, and weak interactions between the Hg atom and Se atoms of neighboring "square planar" molecules.

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Supplementary Material Available: Tables of crystal data, thermal parameters, hydrogen atom positions, and calculations of torsional angles and least squares planes and ORTEP figures for **1** and **2** (13 pages) are available. Ordering information is given on any current masthead page. Structure factor listings are available from the authors.

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