

Pyridineselenolate Complexes of Copper and Indium: Precursors to CuSe_x and In₂Se₃

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The pyridineselenolate (2-Se-NC₅H₄, (SePy)) and the 3-(trimethylsilyl)pyridineselenolate (3-Me₃Si-2-Se-NC₅H₄ (SePy*)) ligands form air-stable homoleptic coordination compounds of Cu(I) { [Cu(SePy)]₄ (**1**) and [Cu(SePy*)]₄ (**2**)} and In(III) {In(SePy)₃ (**3**) and In(SePy*)₃ (**4**)}. Mass spectroscopic characterization of the Cu(I) compounds indicated a tetrametallic core, and this was confirmed with a single-crystal X-ray structural characterization of crystalline **1** and **2**, which both contain a tetrametallic cluster of Cu(I) ions bound to two doubly bridging Se atoms and a pyridine nitrogen. The Cu coordination sphere is completed with two strong Cu–Cu bonds and one weaker Cu–Cu interaction. The indium compounds **3** and **4** are each distorted *fac*-octahedral molecules with chelating SePy ligands. These compounds are useful low-temperature precursors to the binary selenides. Both **3** and **4** sublime intact; **3** thermally decomposes to give In₂Se₃. The Cu clusters do not sublime intact but still decompose to give metal selenide phases: **2** decomposes to give pure α-CuSe at low temperatures and increasing amounts of Cu_{2–x}Se at elevated temperatures, while **3** decomposes to give a mixture of CuSe phases at all temperatures. Crystal data (Mo Kα: **1**, 153(5) K; **2–4**, 293(2) K) are as follows: **1**, monoclinic space group *C2/c*, *a* = 20.643(5) Å, *b* = 16.967(2) Å, *c* = 16.025(2) Å, β = 114.16(2)°, *Z* = 8; **2**, tetragonal space group *I4₁/a*, *a* = 14.756(3) Å, *c* = 19.925(3) Å, *Z* = 4; **3**, trigonal space group *P3c1*, *a* = 13.352(2) Å, *c* = 13.526(2) Å, *Z* = 4; **4**, monoclinic space group *P2₁/c*, *a* = 9.793(1) Å, *b* = 20.828(6) Å, *c* = 16.505(1) Å, β = 96.69(1)°, *Z* = 4.

Introduction

The chalcogenolate chemistry of the main group elements continues to attract considerable attention because main group chalcogenolates are potentially useful as single-source precursors for the low-temperature synthesis of semiconductor materials and because the bonding between metals and the heavier chalcogens is relatively unexplored.^{1–3} The synthesis and

characterization of molecules that decompose to deliver II–VI (i.e. HgTe) semiconductor materials¹ have received the bulk of this attention, although IV–VI² and I–III–V³ systems have also been examined. The ternary I–III–VI systems are important primarily because of their utility in solar energy devices.⁴

Pyridinechalcogenolate (2-E-NC₅H₄ (E = S, Se, Te), (EPy)) ligands are ideal for preparing useful chemical vapor deposition (CVD) sources of chalcogenide-based materials because the bifunctional design imparts both stability and complex volatility. Molecular stability is enhanced because there are both hard/ionic and soft/covalent resonance descriptions that can contribute to the overall stability of M(EPy)_x coordination complexes. These materials can be described either as metal–chalcogenolate compounds with attached pyridine donors or as metal amido complexes with a C=E functional group. In sulfur chemistry,⁵ the later resonance description of pyridinethiolates as hard, ionic ligands accounts for the stability of certain metal complexes in what would otherwise be unusually high oxidation states for a homoleptic thiolate compound, i.e. Tl(III),^{5a} Rh(III),^{5f} Pt(III),^{5a} and Eu(III).^{5s} Molecular volatility is enhanced because the covalently attached nitrogen donor remains tethered throughout the sublimation process, and coordinatively saturated gas-phase species result.

Structurally, EPy ligands are interesting because the two heteroatom donors create a variety of potential bonding modes.

[⊗] Abstract published in *Advance ACS Abstracts*, November 15, 1996.

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The SPy ligand has been studied extensively in this regard, and the wide variety of M–SePy bonding modes in the divalent semiconductor precursors Cd(SePy)₂, Hg(SePy)₂, and [Sn(SePy)₂]₂ is a strong indication that the structural diversity of the analogous Se compounds will be equally rich. In this paper, SePy chemistry is extended to Cu(I) and In(III) semiconductor precursors. The synthesis and structural chemistry of homoleptic CuSePy and In(SePy)₃ compounds are described, and the utility of these molecules in the low-temperature synthesis of In₂Se₃ and CuSe_x is presented.

Experimental Section

General Methods. All syntheses were carried out under ultrapure nitrogen (JWS), using conventional drybox or Schlenk techniques. Solvents (Fisher) were refluxed continuously over molten alkali metals or sodium/benzophenone and collected immediately prior to use. Cu and In were purchased from Strem. Melting points were taken in sealed capillaries and are uncorrected. Powder diffraction spectra were obtained from a Scintag Pad V diffractometer with monochromatized Cu K α radiation. EIMS data were recorded on a Finnigan MAT 8230 mass spectrometer (Mass Spectroscopy Support Facility, Rutgers CAFT). GCMS data were collected on 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 performed by Quantitative Technologies, Inc. (Salem, NJ). Pyridineselenol,¹⁹ dipyridinediselenide,²⁶ and (3-Me₃Si-2-SeNC₅H₃)₂^{2c} were prepared according to literature procedures.

Synthesis of [Cu(2-SeNC₅H₄)]₄ (1). Cu powder (0.10 g, 1.6 mmol) and dipyridinediselenide (0.30 g, 0.96 mmol) were added to toluene (10 mL), and the mixture was refluxed for 12 h to give a yellow precipitate which was collected, washed with acetone, and dried to give a yellow powder (0.32 g, 93%; mp 203–205 °C (dec)). The compound (0.2 g) can be solubilized by addition of excess PPh₃ in CH₂Cl₂ (10 mL) and recrystallized as the phosphine free material by layering with hexane (15 mL) to give yellow-green crystalline **1** (0.08 g). The compound crystallizes as a dichloromethane solvate. Anal. Calcd for Cu_{5.125}H_{4.25}NCl_{0.25}Se: C, 26.6; H, 1.85; N, 6.06. Found: C, 26.8; H, 1.60; N, 5.97. ¹H NMR (DMSO-*d*₆): (1H, 8.16 (d)), (1H, 7.64 (d)), (1H, 7.41 (m)), (1H, 7.08 (m)). The compound does not sublime intact. EIMS: *m/e* 882 (M⁺). IR (KBr): 1579 (s), 1545 (s), 1448 (s), 1410

(s), 1270 (s), 1220 (w), 1150 (s), 1112 (s), 1079 (s), 1046 (s), 1008 (m), 988 (w), 954 (w), 884 (m), 809 (w), 755 (s), 731 (m), 695 (s), 641 (w), 474 (s), 405 (s) cm⁻¹.

Synthesis of [Cu(3-Me₃Si-2-SeNC₅H₃)]₄ (2). Cu powder (70 mg, 1.1 mmol) and di-3-TMS-pyridinediselenide (0.20 g, 0.44 mmol) were added to toluene (5 mL), and the mixture was refluxed for 12 h to give a green solution. The solution was filtered, the solvent was removed under vacuum, and the green powder was washed with cold acetone (30 mL) and then dissolved in CH₂Cl₂ (30 mL). Yellow-green crystals (0.18 g, 78%; mp 209–12 °C (dec)) were obtained by slow evaporation of the solvent over a 2 day period. Anal. Calcd for C₈H₁₂NSeSiCu: C, 32.8; H, 4.13; N, 4.78. Found: C, 32.4; H, 3.92; N, 4.53. ¹H NMR (CDCl₃): (1H, 8.09 (d of d; J₁ = 5.2 Hz, J₂ = 1.8 Hz)), (1H, 7.37 (d of d; J₁ = 7.2 Hz, J₂ = 1.8 Hz)), (1H, 6.84 (d of d; J₁ = 7.2 Hz, J₂ = 5.2 Hz)). LSIMS: *m/e* 1174 (M⁺). IR (KBr): 3447 (s), 3028 (m), 2953 (s), 2895 (m) 2364 (w), 2338 (w), 1944 (w), 1910 (w), 1876 (w), 1557 (s), 1543 (s), 1408 (w), 1354 (s), 1246 (s), 1197 (m), 1127 (s), 1116 (s), 1067 (s), 1045(m), 1001 (w), 940 (w), 843 (s), 792 (m), 757 (s), 688 (m), 671 (m), 624 (m), 501 (w), 452 (w), 405 (s) cm⁻¹.

Attempted Synthesis of Cu(2-SeNC₅H₄)₂. Pyridine-2-selenol (1.0 g, 6.33 mmol) was added to a solution of Cu(OAc)₂ (0.575 g, 3.17 mmol) in methanol (50 mL), and the mixture was stirred under ultrapure nitrogen for 3 h. The solution was filtered, and the solvent was removed under vacuum to give yellow dipyridinediselenide that was identified by ¹H NMR and melting point. The yellow precipitate was washed with petroleum ether (100 mL) and cold water (200 mL) and then dried to give **1** (0.64 g, 92%) that was identified by melting point and ¹H NMR.

Synthesis of In(2-SeNC₅H₄)₃ (3). Indium powder (0.12 g, 1.05 mmol) and dipyridinediselenide (0.50 g, 1.59 mmol) were added to toluene (10 mL), and the mixture was refluxed for 12 h to give a yellow precipitate. The solid was isolated by filtration and dissolved in acetone (50 mL). Filtration of the solution, followed by slow evaporation of the acetone, gave yellow crystals (0.53 g, 86%) that were collected and washed with cold hexane (100 mL). The compound crystallizes with a lattice acetone that desolvates over a period of days. Anal. Calcd for C₁₅H₁₂N₃InSe₃: C, 30.7; H, 2.06; N, 7.17. Found: C, 30.7; H, 1.99; N, 7.06. The compound sublimates at 193 °C (0.1 mmHg) without decomposition and decomposes at 236–238 °C. ¹H NMR (CDCl₃): (2H, 7.63 (m), (1H, 7.47 (m), (1H, 7.02 (m)). IR (KBr): 1580 (s), 1543 (s), 1441 (s), 1414 (s), 1262 (s), 1235 (m), 1147 (m), 1120 (s), 1075 (m), 1041 (m), 1003 (m), 874 (w), 803 (w), 758 (s), 728 (w), 697 (m), 640 (m), 601 (w), 470 (m), 407 (m) cm⁻¹.

Synthesis of In(3-Me₃Si-2-SeNC₅H₃)₃ (4). Indium powder (33 mg, 0.29 mmol) and di-3-TMS-pyridinediselenide (0.20 g, 0.44 mmol) were added to toluene (5 mL), and the mixture was refluxed for 12 h. The solvent was removed under vacuum, and the yellow solid was extracted with hexane (30 mL). Filtration of the solution, followed by slow evaporation of the hexane, gave yellow crystals (0.15 g, 65%). Anal. Calcd for InC₂₄H₃₆N₃Se₃Si₃: C, 35.9; H, 4.52; N, 5.24. Found: C, 35.8; H, 4.37; N, 5.20. The compound sublimates at 214 °C (0.1 mmHg) without decomposition and melts at 234–237 °C. EIMS: *m/e* 668.0 (M⁺). ¹H NMR (CDCl₃): (1H, 8.40 (m), (1H, 7.59 (m), (1H, 7.02 (m)). IR (KBr): 2952 (s), 2855 (s), 1581 (w), 1560 (s), 1541 (s), 1461 (s), 1376 (s), 1360 (s), 1249 (s), 1222 (m), 1129 (m), 1113 (m), 1067 (m), 1043 (w), 846 (s), 796 (m), 759 (s), 723 (w), 695 (w), 664 (s), 627 (m), 405 (m) cm⁻¹.

Thermolysis. All thermolysis samples were sealed in an evacuated tube, and the temperature was raised slowly over a period of hours. One end of the thermolysis tube was kept at room temperature outside of the oven. The Cu compounds decompose to give either α -CuSe or Cu_{2–x}Se, depending on the thermolysis conditions. In the thermolysis of **2** (0.50 g, 1.70 mmol) at 220 °C for 3 h, X-ray powder diffraction (XRPD) showed that Cu_{2–x}Se (0.18 g) was the only crystalline phase present. The thermolysis of **2** for 3 h at 250 °C gave a mixture of α -CuSe and Cu_{2–x}Se. In contrast, the thermolysis of **1** always gave a mixture of α -CuSe and Cu_{2–x}Se. At 210 °C, **1** decomposes to give α -CuSe and Cu_{2–x}Se, and at 270 °C, the XRPD profile due to α -CuSe increases in intensity relative to the Cu_{2–x}Se profile. At 400 °C, elemental Se begins to condense in the RT zone of the thermolysis tube. All of the Cu thermolysis experiments produce a mixture of

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Table 1. Crystal Data and Structure Refinement for [Cu(SePy)]₄ (**1**), [Cu(SePy*)]₄ (**2**), In(SePy)₃ (**3**), and In(SePy*)₃ (**4**)

	compound			
	1	2	3	4
empirical formula	C _{20.5} H ₁₇ ClCu ₄ N ₄ Se ₄	C ₈ H ₁₂ CuNSeSi	C ₅ H ₄ In _{0.33} NSe(C ₃ H ₆ O) _{0.5}	C ₂₄ H ₃₆ N ₃ Se ₃ Si ₃ In
fw	924.83	292.78	224.36	802.53
space group	C2/c (No. 15)	I4 ₁ /a (No. 88)	P3c1 (No. 165)	P2 ₁ /c (No. 14)
a (Å)	20.643(5)	14.756(3)	13.352(2)	9.793(1)
b (Å)	16.967(2)	14.756(3)	13.352(2)	20.828(6)
c (Å)	16.025(2)	19.925(3)	13.562(2)	16.505(1)
α (deg)	90	90	90	90
β (deg)	114.16(2)	90	90	96.69(1)
γ (deg)	90	90	120	90
V (Å ³)	5121(2)	4338(1)	2088.3(5)	3344(1)
Z	8	16	12	4
D(calcd) (Mg/m ³)	2.399	1.793	2.141	1.594
temp (K)	153(5)	293(2)	293(2)	293(2)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
abs coeff (mm ⁻¹)	9.09	5.43	6.37	4.10
obsd reflns [I > 2σ]	3245	1198	636	3144
final R(F) [I > 2σ] ^a	0.035	0.046	0.041	0.034
wR(F ²) indices [I > 2σ]	0.079	0.120	0.068	0.066

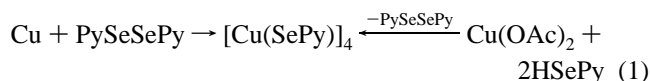
^a Definitions: $R(F_o) = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR(F_o^2) = \{\sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)]^2\}^{1/2}$. Additional crystallographic details are given in the Supporting Information.

organic products that include pyridine, SePy₂, and PySeSePy. The In compound **3** (0.5 g, 0.85 mmol) was also heated to 220 °C for 3 h, and an XRPD analysis of the final solid state product indicated that In₂Se₃ (0.18 g, 3.93 mmol, 92%) was the only crystalline phase present.

X-ray Crystallography of 1–4. Data for **1–4** were collected on a CAD4 diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å) at room temperature. The check reflections measured every 2 h showed less than 2% intensity variation. The data were corrected for Lorentz effects and polarization and absorption, the latter by a numerical (SHELX76)⁶ method. The structures were solved by Patterson methods (SHELXS86).⁷ All non-hydrogen atoms were refined (SHELXL93)⁸ on the basis of F_o². All hydrogen atom coordinates were calculated with idealized geometries (SHELXL93). The crystal structure of **1** contained some disorder such that a minor component (<7%) of the complex was found to occupy the same volume as the major component (x, y, z) but at a position approximately 0.37 - x, y, 0.35 - z. The geometry of the minor component was refined but restrained within an estimated standard deviation of 0.01 Å to have the same intramolecular distances as the major component. Scattering factors (f_o, f', f'') are as described in SHELXL93. Crystallographic data and final R indices for all three compounds are given in Table 1. Significant bond distances and angles for **1–4** are given in Tables 2–5, respectively. Complete crystallographic details are given in the Supporting Information. ORTEP diagrams⁹ of the molecules are shown in Figures 1–4. Thermal ellipsoids are shown at the 50% probability level.

Results

The synthesis of homoleptic copper(I) pyridineselenolate complexes can be approached either by starting with elemental Cu and PySeSePy or by the proton transfer reaction of HSePy with Cu(OAc)₂ in methanol (reaction 1). In the proton transfer



reaction, reduction of the metal from Cu(II) to Cu(I) and formation of dipyridyldiselenide is a clear indication that the

Table 2. Significant Bond Lengths (Å) and Angles (deg) for **1**

Cu(1)–N(4)	1.995(5)	Cu(1)–Se(2)	2.360(1)
Cu(1)–Se(1)	2.377(1)	Cu(1)–Cu(4)	2.600(1)
Cu(1)–Cu(2)	2.658(1)	Cu(1)–Cu(3)	2.815(1)
Cu(2)–N(1)	2.006(5)	Cu(2)–Se(3)	2.362(1)
Cu(2)–Se(2)	2.385(1)	Cu(2)–Cu(3)	2.617(1)
Cu(2)–Cu(4)	2.778(1)	Cu(3)–N(2)	2.008(5)
Cu(3)–Se(4)	2.385(1)	Cu(3)–Se(3)	2.390(1)
Cu(3)–Cu(4)	2.632(1)	Cu(4)–N(3)	2.017(5)
Cu(4)–Se(1)	2.377(1)	Cu(4)–Se(4)	2.392(1)
Se(1)–C(1)	1.919(6)	Se(2)–C(6)	1.922(7)
Se(3)–C(11)	1.919(7)	Se(4)–C(16)	1.924(6)
N(4)–Cu(1)–Se(2)	123.1(2)	N(4)–Cu(1)–Se(1)	114.1(2)
Se(2)–Cu(1)–Se(1)	121.61(4)	N(4)–Cu(1)–Cu(4)	100.5(2)
Se(2)–Cu(1)–Cu(4)	118.18(4)	Se(1)–Cu(1)–Cu(4)	56.85(3)
N(4)–Cu(1)–Cu(2)	149.5(2)	Se(2)–Cu(1)–Cu(2)	56.39(3)
Se(1)–Cu(1)–Cu(2)	80.37(4)	Cu(4)–Cu(1)–Cu(2)	63.78(4)
N(4)–Cu(1)–Cu(3)	92.5(2)	Se(2)–Cu(1)–Cu(3)	77.01(4)
Se(1)–Cu(1)–Cu(3)	112.59(4)	Cu(4)–Cu(1)–Cu(3)	58.00(3)
Cu(2)–Cu(1)–Cu(3)	57.05(3)	N(1)–Cu(2)–Se(3)	126.4(2)
N(1)–Cu(2)–Se(2)	107.8(2)	Se(3)–Cu(2)–Se(2)	124.70(5)
N(1)–Cu(2)–Cu(3)	152.2(2)	Se(3)–Cu(2)–Cu(3)	57.09(3)
Se(2)–Cu(2)–Cu(3)	80.65(4)	N(1)–Cu(2)–Cu(1)	97.8(2)
Se(3)–Cu(2)–Cu(1)	118.95(4)	Se(2)–Cu(2)–Cu(1)	55.50(3)
Cu(3)–Cu(2)–Cu(1)	64.50(3)	N(1)–Cu(2)–Cu(4)	94.3(2)
Se(3)–Cu(2)–Cu(4)	77.62(4)	Se(2)–Cu(2)–Cu(4)	110.89(4)
Cu(3)–Cu(2)–Cu(4)	58.31(3)	Cu(1)–Cu(2)–Cu(4)	57.11(3)
N(2)–Cu(3)–Se(4)	122.3(2)	N(2)–Cu(3)–Se(3)	114.6(2)
Se(4)–Cu(3)–Se(3)	122.07(4)	N(2)–Cu(3)–Cu(2)	100.3(2)
Se(4)–Cu(3)–Cu(2)	118.61(4)	Se(3)–Cu(3)–Cu(2)	56.08(3)
N(2)–Cu(3)–Cu(4)	148.7(2)	Se(4)–Cu(3)–Cu(4)	56.69(3)
Se(3)–Cu(3)–Cu(4)	80.14(4)	Cu(2)–Cu(3)–Cu(4)	63.92(4)
N(2)–Cu(3)–Cu(1)	91.9(2)	Se(4)–Cu(3)–Cu(1)	76.76(4)
Se(3)–Cu(3)–Cu(1)	112.22(4)	Cu(2)–Cu(3)–Cu(1)	58.45(3)
Cu(4)–Cu(3)–Cu(1)	56.92(3)	N(3)–Cu(4)–Se(1)	126.0(2)
N(3)–Cu(4)–Se(4)	108.4(2)	Se(1)–Cu(4)–Se(4)	124.00(4)
N(3)–Cu(4)–Cu(1)	153.3(2)	Se(1)–Cu(4)–Cu(1)	56.83(3)
Se(4)–Cu(4)–Cu(1)	80.99(4)	N(3)–Cu(4)–Cu(3)	98.7(2)
Se(1)–Cu(4)–Cu(3)	119.35(4)	Se(4)–Cu(4)–Cu(3)	56.44(3)
Cu(1)–Cu(4)–Cu(3)	65.08(3)	N(3)–Cu(4)–Cu(2)	94.6(2)
Se(1)–Cu(4)–Cu(2)	77.90(4)	Se(4)–Cu(4)–Cu(2)	112.44(4)
Cu(1)–Cu(4)–Cu(2)	59.11(3)	Cu(3)–Cu(4)–Cu(2)	57.78(3)

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(9) Johnson, C. K. ORTEPII; Report ORNL-5138. Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

cupric ion will not form a stable homoleptic SePy complex. Both [Cu(SePy)]₄ (**1**) and [Cu(SePy*)]₄ (**2**) have been isolated and characterized by mass spectroscopy to establish product nuclearity: Both compounds give a parent ion for a tetrametallic cluster, although neither compound sublimes completely intact. Examination of both **1** and **2** by single-crystal X-ray diffraction

Table 3. Significant Bond Lengths (Å) and Angles (deg) for **2^a**

Cu–N	2.022(5)	Cu–Se	2.344(1)
Cu–Se'	2.403(1)	Cu–Cu''	2.600(1)
Cu–Cu'	2.600(1)	Cu–Cu'''	2.861(2)
Se–C	1.918(6)	Se–Cu''	2.403(1)
N–Cu–Se	122.9(2)	N–Cu–Se'	111.9(2)
Se–Cu–Se'	124.73(4)	N–Cu–Cu''	101.5(2)
Se–Cu–Cu''	57.88(4)	Se'–Cu–Cu''	119.49(4)
N–Cu–Cu'	142.2(2)	Se–Cu–Cu'	82.62(4)
Se'–Cu–Cu'	55.71(3)	Cu''–Cu–Cu'	66.77(3)
N–Cu–Cu'''	86.46(14)	Se–Cu–Cu'''	111.90(3)
Se'–Cu–Cu'''	76.23(4)	Cu''–Cu–Cu'''	56.61(2)
Cu'–Cu–Cu'''	56.61(2)	C–Se–Cu	111.8(2)
C–Se–Cu''	96.1(2)	Cu–Se–Cu''	66.41(4)

^a Symmetry transformations used to generate equivalent atoms: ', $y - 1/4, -x + 1/4, -z + 1/4$;'', $-y + 1/4, x + 1/4, -z + 1/4$;''', $-x + 1 - 1, -y + 1/2, z + 1 - 1$.

Table 4. Significant Bond Lengths (Å) and Angles (deg) for **3^a**

In–N	2.343(6)	In–Se	2.656(1)
Se–C(1)	1.9144(7)		
C(1)–Se–In	78.1(3)	N'–In–N	86.0(2)
N–In–Se''	149.1(2)	N–In–Se'	103.8(2)
N–In–Se	66.0(2)	Se''–In–Se	106.94(3)

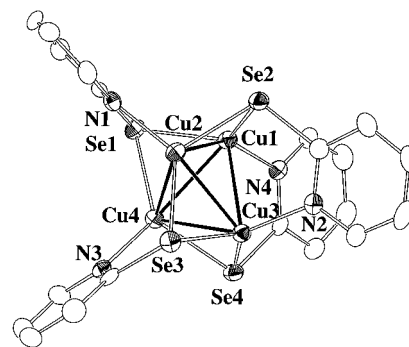
^a Symmetry transformations used to generate equivalent atoms: ', $-y + 1, x - y + 1, z$;'', $-x + y, -x + 1, z$.

Table 5. Significant Bond Lengths [Å] and Angles (deg) for **4**

In–N(1)	2.320(4)	In–Se(1)	2.652(1)
In–N(2)	2.317(4)	In–Se(2)	2.650(1)
In–N(3)	2.342(4)	In–Se(3)	2.643(1)
Se(1)–C(1)	1.897(5)	Se(2)–C(9)	1.894(5)
Se(3)–C(17)	1.906(5)		
N(2)–In–N(1)	86.8(1)	N(1)–In–Se(3)	99.3(1)
N(2)–In–N(3)	85.0(2)	N(3)–In–Se(3)	65.6(1)
N(1)–In–N(3)	89.0(2)	N(2)–In–Se(3)	149.7(1)
Se(3)–In–Se(2)	109.37(3)	N(2)–In–Se(2)	66.1(1)
Se(2)–In–Se(1)	108.19(3)	N(1)–In–Se(2)	150.9(1)
Se(3)–In–Se(1)	108.14(2)	N(3)–In–Se(2)	98.4(1)
N(2)–In–Se(1)	101.4(1)	N(3)–In–Se(1)	153.0(1)
N(1)–In–Se(1)	65.5(1)		

confirms the tetrametallic formulation. The molecular structure of **2** was solved in the second origin choice (at the $\bar{1}$) space group $I4_1/a$ (No. 88). Both **1** and **2** contain a tetrahedral array of Cu(I) ions held together by a series of Cu–Cu bonds. A half methylene chloride molecule of solvation was also found in the crystallographic asymmetric unit of **1**. The triangular faces of the tetrahedron are capped with PySe ligands, where the Se atoms each bridge a pair of Cu atoms, and the nitrogen donor coordinates to the third facial Cu. In addition to the two Cu–Se bonds and one Cu–N bond per metal ion, there are also distinct Cu–Cu bonds in both **1** (Cu(1)–Cu(4), 2.600(1) Å; Cu(1)–Cu(2), 2.658(1) Å; Cu(1)–Cu(3), 2.815(1) Å; Cu(2)–Cu(3), 2.617(1) Å; Cu(2)–Cu(4), 2.778(1) Å; Cu(3)–Cu(4) 2.632(1) Å) and in **2** (Cu(1)–Cu(1)'', 2.600(1) Å; Cu(1)–Cu(1)', 2.600(1) Å; Cu(1) Cu(1)''', 2.861(2) Å).

Both SePy and SePy* form stable, crystalline coordination complexes with In(III). The unsubstituted derivative In(SePy)₃ (**3**) crystallizes from acetone as a distorted *fac*-octahedral molecule with a crystallographically imposed 3-fold axis that relates all three In–N and all three In–Se bonds. A half acetone molecule of solvation was also found in the crystallographic asymmetric unit of **3**. The silylated derivative In(SePy*)₃ (**4**), which crystallizes from hexane, also adopts a *fac*-octahedral geometry. The addition of a Me₃Si group has a negligible influence on the bond geometries of the In compounds. Related bond lengths and angles in the two In structures are essentially

**Figure 1.** Molecular structure of [Cu(SePy)]₄ (**1**).

identical. These two In compounds do not appear to react with the Cu compounds to form heterometallic products. A heterometallic precipitate does form in the one pot reduction of PySeSePy with both Cu and In, but the product is completely insoluble in strong donor solvents.

The title molecules can be used in the low-temperature synthesis of the corresponding solid-state metal selenides. Thermal decomposition of either **1** or **2** under reduced pressure generally gives a mixture of α -CuSe¹⁰ and Cu_{2-x}Se.¹¹ The silylated derivative **2** was the only compound that gave pure α -CuSe at lower temperatures, while at higher temperatures a mixture of CuSe phases were observed. Compound **1** was found to give a mixture of both α -CuSe and Cu_{2-x}Se at all temperatures studied. At higher temperatures these CuSe phases tend to lose elemental Se that condenses in the cold part of the thermolysis tube. Decomposition of the indium compound **3** gives solid-state In₂Se₃.¹²

Discussion

Both Cu and In complexes are best prepared by direct insertion of the elemental metal into the diselenide bond, as has been noted previously in the syntheses of main group thiolates and selenolates. The tetrametallic Cu compounds [Cu(SePy)]₄ (**1**) and [Cu(3-Me₃Si-2-SeNC₅H₄)]₄ (**2**) are considerably less soluble than the In compounds, and the non-silylated derivative **1** is sparingly soluble in pyridine and insoluble in other common organic solvents. The same compound is also isolated from the proton transfer reaction of HSePy with Cu(OAc)₂, which is consistent with previous work indicating that even the more electronegative pyridinethiolate ligands are incapable of forming a stable homoleptic Cu^{II}(SPy)₂ compound. Attaching a Me₃Si group at the 3 position of the pyridine ring imparts hexane solubility to the homoleptic Cu(I) compound and readily facilitates crystallization from nondonor solvents.

Both **1** (Figure 1) and **2** (Figure 2) have the same general structure, with a tetrahedral array of Cu(I) ions connected through a series of Cu–Cu bonds and selenolate ligands that each bridge two metal centers. There are a number of structurally characterized chalcogenolate complexes of Cu, all of which differ considerably from the structures of **1** and **2**. The most appropriate comparison is between the analogous pyridinethiolate complexes [Cu(SPy)]₆¹³ and [Cu(3-Me₃Si-2-SNC₅H₄)]₆¹⁴ which crystallize in a hexametallc array containing pseudo-trigonal planar Cu(I) ions, doubly bridging sulfur atoms,

(10) JCPDS file 20-1020, 27-0184.

(11) JCPDS file 06-0680.

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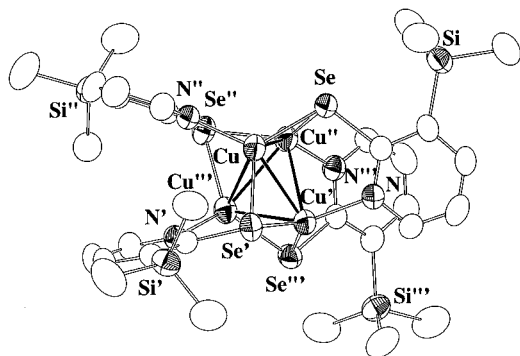


Figure 2. Molecular structure of $[\text{Cu}(\text{SePy}^*)]_4$ (2).

and a nitrogen donor that completes the Cu coordination sphere. Both of these pyridineselenolate structures show considerably less Cu–Cu bonding that found in the selenolate derivatives **1** and **2**.

The structures of two Cu(I) selenolates, $[(\text{PCy}_3)\text{CuSeC}(\text{SiMe}_3)_3]_2^{3f}$ and $(\text{Ph}_3\text{P})_2\text{Cu}(\text{SeEt})_2\text{In}(\text{SeEt})_2^{3a}$, have been reported in the literature, in which additional neutral donor ligands were used to saturate the Cu(I) coordination sphere and solubilize the CuSeR group. In each case, the presence of a stronger phosphine donor resulted in the formation of compounds with no Cu–Cu bonds.

It is also appropriate to compare the structure of $[\text{CuSePy}]_4$ with the numerous halide adducts of Cu(I).¹⁵ LCuX compounds have a diverse structural chemistry (dimers, tetramers, polymers, cation/anion pairs) in which structure is dependent on the steric and electronic properties of L, as well as the identity of the halogen, X. These molecules are particularly interesting from the perspective of determining whether the Cu–Cu distances in these d^{10} – d^{10} compounds are bonding interactions; e.g. in dimeric Cu(I)–Cu(I) compounds, Cu–Cu single bond orders have been convincingly described.¹⁶ A direct comparison of **1** and **2** with the numerous $[\text{LCuX}]_4$ structures is unfortunately complicated by the unusual ligation of these pseudohalide ligands—in LCuX tetramers, the halide ligands generally bridge three metal centers, while in the present compounds the selenolate bridges to only two Cu(I) ions. Still, the short Cu–Cu bonds in **1** (2.62(1), 2.63(1) Å) and **2** (2.600(1) Å) are among the shortest Cu–Cu interactions of the known Cu(I) tetramers for which Cu–Cu bonds are evident, (i.e. in $[\text{Cu}(\text{NC}_5\text{H}_{11})_4]_4^{15a}$ Cu–Cu = (2.630(2) Å, 2.671(2) Å); in $[\text{Cu}(\text{NC}_5\text{H}_5)_4]_4^{15d}$ 2.690(5) Å, 2.684(5) Å) and directly contrast the lack of bonding interactions (Cu–Cu > 3.0 Å) in complexes such as $[\text{Et}_3\text{P}\cdot\text{CuCl}]_4^{15l}$ and $[\text{PET}_3\cdot\text{CuI}]_4^{15m}$

(15) (a) Schramm, V. *Cryst. Struct. Commun.* **1982**, *11*, 1549. (b) Schramm, V. *Cryst. Struct. Commun.* **1980**, *9*, 1231. (c) Schramm, V. *Inorg. Chem.* **1978**, *17*, 714. (d) Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1976**, 2153. (e) Dyason, J. C.; Healy, P. C.; Engelhardt, L. M.; Pakawatchai, C.; Patrick, V. A.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1985**, 831. (f) Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* **1974**, *13*, 1899. (g) Healy, P. C.; Pakawatchai, C.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 1905. (h) Barron, P. F.; Dyason, J. C.; Engelhardt, L. M.; Healy, P. C.; White, A. H. *Inorg. Chem.* **1984**, *23*, 3766. (i) Rath, N. P.; Holt, E. M.; Tanimura, K. *Inorg. Chem.* **1985**, *24*, 3934. (j) Schaefer, W. P. *Inorg. Chem.* **1986**, *25*, 2665. (k) Goel, R. G.; Beauchamp, A. L. *Inorg. Chem.* **1983**, *22*, 395. (l) Churchill, M. R.; Davies, G.; El-Sayed, M. A.; Hutchinson, J. P.; Rupich, M. W. *Inorg. Chem.* **1982**, *21*, 995. (m) Churchill, M. R.; DeBoer, B. G.; Mendak, S. J. *Inorg. Chem.* **1975**, *14*, 2041. (n) Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* **1974**, *13*, 1899. (o) Churchill, M. R.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 3267. (p) Engelhardt, L. M.; Healy, P. C.; Kildea, J. D.; White, A. H. *Aust. J. Chem.* **1989**, *42*, 107.

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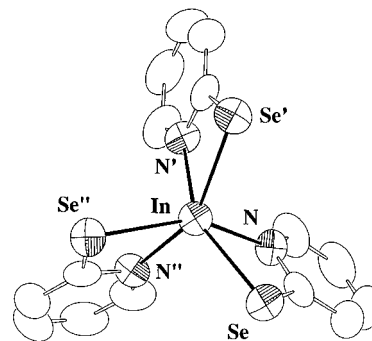


Figure 3. Molecular structure of $\text{In}(\text{SePy})_3$ (3).

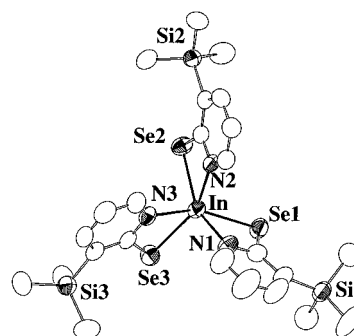


Figure 4. Molecular structure of $\text{In}(\text{SePy}^*)_3$ (4).

The structures of the In compounds **3** (Figure 3) and **4** (Figure 4) are relatively straightforward, with both containing chelating pyridineselenolate ligands in a distorted *fac*-octahedral geometry, similar to the corresponding thiolate derivatives.¹⁷ Both the Cu and In structures represent new bonding modes for the pyridineselenolate ligand. The chelating ligation found in **3** and **4** is similar to the chelating SePy interaction in $[\text{Sn}(\text{SePy})_2]_2$, although in the tin structure there was an additional weak interaction between the Se atom on the chelating ligand and a Sn atom in a neighboring dimeric unit. Similarly, in $\text{Hg}(\text{SePy})_2$, the “chelating” SePy ligands are oriented such that there is a weak, but distinct, interaction between the Se and neighboring Hg(II) ions. A second notable difference between the SePy bonding modes in the Hg and two In structures can be found in the M–N bonds, where the Hg–N bond appears to be relatively uninvolved in bonding with the *sp* hybridized Hg(II) ion, while in the In(III) structures the In–N bond lengths clearly indicate that the In–N interactions are significant. The SePy bonding in the Cu structure has no parallel in the structures of $[(\text{BIPY})\text{Li}(\text{SePy})_2]_2^{18}$, $\text{Sn}(\text{SePy})_2^{2c}$, $\text{Cd}(\text{SePy})_2$, or $\text{Hg}(\text{SePy})_2^{19}$

Because the photophysical properties of CuInSe_2 are particularly well suited for solar energy applications, it was important to examine the potential utility of these molecules as CVD precursors. Thermolysis of the In compound **3** proceeded as expected (on the basis of related experiments with Cd(II), Hg(II), Sn(II), Sn(IV), and Pb(II) SePy complexes). Compound **3** sublimes intact and decomposes at elevated temperatures to give In_2Se_3 . The Cu compounds unfortunately do not sublime intact but instead sublime with partial decomposition (a parent ion is observed in the mass spectrum). The Cu compounds decompose to give CuSe, CuSe_2 , or mixtures of the two phases, depending on the thermolysis conditions. In related thiolate chemistry,

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Cu(SC₅F₅) behaved similarly, giving a mixture of sulfide phases that were identified as CuS·4Cu₂S.¹⁹

In contrast to the ethaneselenolates of Cu and In, the pyridyselenolates of Cu and In do not react with each other to form heterometallic chalcogenolates. This nonreactivity can be attributed to the presence of the pyridine donors, which compete effectively with bridging selenolate ligands for access to the metal coordination sphere to form molecular In compounds and to the stabilizing influence of the Cu–Cu bonds in the Cu compounds. When PySeSePy is reduced with a mixture of Cu and In, molecular compounds are not isolated and instead a white precipitate forms. All efforts to solubilize and subsequently crystallize this material were unsuccessful. This

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heterometallic material is nonvolatile and thus unsuitable for CVD applications.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, under Grant 26123-G3. We thank Dr. Bob Rosen (Rutgers Center for Food Technology) for providing the mass spectra.

Supporting Information Available: Tables of crystallographic details and refinement results, atomic coordinates and *U* values, complete bond lengths and angles, anisotropic displacement parameters, and hydrogen atom parameters, fully labeled ORTEP diagrams for **1–4**, and X-ray powder diffraction profiles for the thermolysis products of **1–3** (18 pages). Ordering information is given on any current masthead page.

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