Pyridineselenolate Complexes of Tin and Lead: Sn(2-SeNC₅H₄)₂, Sn(2-SeNC₅H₄)₄, Pb(2-SeNC₅H₄)₂, and Pb(3-Me₃Si-2-SeNC₅H₃)₂. Volatile CVD Precursors to Group IV−Group VI Semiconductors

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Pyridineselenolate forms stable homoleptic coordination compounds of Sn(II), Sn(IV), and Pb(II). The complexes can be prepared either by metathesis or by insertion of the metal into the Se−Se bond of dipyridyl diselenide, and they are soluble in coordinating solvents such as pyridine. Isolation of the Pb(II) complex from both Pb(0) and Pb(IV) starting materials indicates that the pyridineselenolate ligand cannot stabilize Pb(IV). The compounds all sublime intact and decompose at elevated temperatures: the divalent complexes give MSe (M = Sn, Pb), while the Sn(IV) compound delivers SnSe₂. In order to isolate a crystalline Pb compound, the 3-trimethylsilyl-2-pyridineselenolate ligand was prepared. Attachment of the Me₃Si functional group increases compound solubility, and leads to the isolation of crystalline Pb(3-Me₃Si-2-SeNC₅H₄)₂. The structure of [Sn(2-SeNC₅H₄)₂]₂ (**1**) was determined by single-crystal X-ray diffraction and shown to be a dimer, with one chelating pyridineselenolate per Sn(II) and a pair of pyridineselenolates that asymmetrically span the two metal centers to form an eight membered (−Sn−Se−C−N−Sn−Se−C−N−) ring, with weak Sn−Se interactions connecting the dimeric units. Crystal data for **1** (Mo Kα, 298(2) K): orthorhombic space group *Pbca*, *a* = 8.214(1) Å, *b* = 21.181(3) Å, *c* = 14.628(2) Å.

Introduction

The chalcogenolate chemistry of the main group elements has recently attracted 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] Compounds of tin and lead are important in this area because the solid state chalco-genides are narrow-band gap semiconductors that are widely used as sensor and laser materials,[2] as thin film polarizers,[3] and as thermoelectric cooling materials.[4]

Early metal chalcogenolate work relied upon the coordination of neutral donor ligands to saturate the metal coordination sphere and make the compound soluble in organic solvents. These neutral donor solvents have a tendency to dissociate from metal chalcogenolate compounds under chemical vapor deposition (CVD) conditions, and this solvent loss results in the formation of polymeric, involatile metal chalcogenolates.[1f−o] Most of the currently employed ligand systems in main group chalcogenolate chemistry use bulky organic substituents[1a−e] to sterically inhibit the coordination of neutral donors and decrease the tendency of chalcogenolates to form polymeric structures, thus enhancing compound solubility and volatility. Complexes with 2,4,6-trisubstituted phenylchalcogenolates and the silylchalcogenolates are notable in this regard. An alternative approach to the synthesis of molecules with ideal physical properties involves the use of bifunctional chalcogenolate ligands[1a,c,p] such as the pyridinechalcogenolates.

Pyridinechalcogenolate (2-E-NC₅H₄ (E = S, Se, Te) or EPy) ligands impart a number of useful physical properties to inorganic molecules. They are ideally suited for preparing stable, volatile, metal chalcogenolate compounds in a variety of oxidation states. Molecular volatility is enhanced because

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(1) (a) Cheng, Y.; Emge, T.; Brennan, J. G. *Inorg. Chem.* **1994,** *33,* 3711. (b) Seligson, A. L.; Arnold, J. *J. Am. Chem. Soc.* **1993,** *115,* 8214. (c) Bonasia, P. J.; Arnold, J. *J. Organomet. Chem.* **1993,** *449,* 147. (d) Bochmann, M.; Bwembya, G.; Grinter, R.; Lu, J.; Webb, K.; Williamson, D. J.; Hursthouse, M. B.; Mazid, M. *Inorg. Chem.* **1993,** *32,* 532. (e) Bochmann, M.; Webb, K.; Harman, M.; Hursthouse, M. B. *Angew. Chem., Int. Ed. Engl.* **1990,** *29,* 638. (f) Osakada, K.; Yamamoto, A. *Inorg. Chem.* **1990,** *30,* 2328. (g) Brennan, J.; Siegrist, T.; Stuczynski, S.; Carroll, C.; Rynders, P.; Brus, L.; Steigerwald, M. *Chem. Mater.* **1990,** *2,* 403. (h) Brennan, J.; Siegrist,T.; Carroll, C.; Stuczynski, S.; Brus, L.; Steigerwald, M. *J. Am. Chem. Soc.* **1989,** *111,* 4141. (i) Osakada K.; Yamamoto, T. *J. Chem. Soc., Chem. Commun.* **1987,** 1117. (j) Steigerwald, M.; Sprinkel, C. *J. Am. Chem. Soc.* **1987,** *109,* 7200. (k) Kern, R. J. *J. Am. Chem. Soc.* **1953,** *75,* 1865. (l) Peach, M. E. *J. Inorg. Nucl. Chem.* **1973,** *35,* 1046. (m) Peach, M. E. *J. Inorg. Nucl. Chem.* **1979,** *41,* 1390. (n) Craig, D.; Dance, I.; Garbutt, R. *Angew. Chem., Int. Ed. Engl.* **1986,** *25,* 165. (o) Berardini, M.; Emge, T. J.; Brennan, J. G. *J. Am. Chem. Soc.* **1994,** *116,* 6941−2. (p) Hursthouse, M. B.; Khan, O.; Mazid, M.; Motevalli, M.; O'Brien, P. *Polyhedron* **1990,** *9,* 541. (q) Shaw, R. A.; Woods, M. *J. Chem. Soc. A,* **1971,** 1569. (r) Dance, I.; Garbutt, R.; Craig, D.; Scudder, M. *Inorg. Chem.* **1987,** *26,* 4057. (s) MacInnes, A. N.; Power, M. B.; Barron, A. R. *Chem. Mater.* **1992,** *4,* 11. (t) Farneth, W. E.; Herron, N.; Wang, Y. *Chem. Mater.* **1992,** *4,* 916. (u) Dance, I.; Garbutt, R.; Craig, D.; Scudder, M. *Inorg. Chem.* **1987,** *26,* 4057. (v) Arnold, A. ; Canty, A.; Skelton, B.; White, A. *J. Chem. Soc., Dalton Trans.* **1982,** 607. (w) Canty, A.; Raston, C.; White, A. *Aust. J. Chem.* **1981,** *34,* 57. (x) Dance, I. G. *J. Am. Chem. Soc.* **1980,** *102,* 3445−3451. (y) Arnold, A. ; Canty, A. *Inorg. Chim. Acta* **1981,** *55,* 171. (z) Hitchcock, P. B.; Lappert, M. F.; Samways, B. J.; Weinberg, E. L. *J. Chem. Soc., Chem. Commun.* **1983,** 1492. (aa) Krautner, G.; Favreau, P.; Nunnally, B. K.; Rees, W. S. *Proc. Mater. Res. Soc.* **1994,** *327,* 41.

(2) (a) Kondas,D. A. *Report* **1993,** ARFSD-TR-92024; Order No. AD-A260781, 26 pp. (b) Zasavitskii, I. I. *Tr. Fiz. Inst. im. P. N. Lebedeva, Ross. Akad. Nauk* **1993,** *224,* 3 (Russian). (c) Keefe, A. UK Pat. Appl. GB 2,249,844. (d) Agranov, G. A.; Novoselov, S. K.; Stepanov, R. M. *Eur. Space Agency ESA SP* **1992,** *ESA SP-356,* 191. (e) Masumoto, K.; Mochizuki, K. Eur. Pat. Appl. EP 535,594, JP Appl.91/251,656. (f) Masumoto, Katashi; Mochizuki, K. Eur. Pat. Appl. EP 551,089, JP Appl. 92/2,307, 09. (g) Dierschke, E. G. U.S. Patent US 5,162,887. (h) Toyoda, M.; Jpn. Kokai Tokkyo, Koho JP 05,327,030 [93,327,030]. (9) Toyoda, Masahiko Jpn. Kokai Tokkyo Koho JP 05,55,638 [93,55,638].
(3) Taga, Y.; Suzuki, M. U.S. Patent 5,305,143; JP Appl.90/212,125, 09.
(4) Harman, T. C. PCT Int. Appl. WO 9,416,465; US Appl. 2,451,12.

the covalently attached nitrogen donor cannot diffuse more than a few angstroms from the central ion, and so the neutral donor functionality remains present up to the sublimation temperature and in the gas phase.

Molecular stability is enhanced because there are two resonance descriptions that can contribute to the overall stability of M(EPy)$_x$ coordination complexes.[5] 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. The latter resonance description of pyridinechalcogenolates as hard, ionic ligands accounts for the stability of certain metal complexes in what would otherwise be unusually high oxidations states for a homoleptic thiolate compound, i.e. Tl(III),[5n] Rh(III),[5f] Pt(III),[5a] and Eu(III).[5s]

Structurally, EPy ligands are interesting because the two heteroatom donors create a variety of potential bonding modes. For example, in pyridinethiolate complexes, the sulfur donor has bridged two metal centers, the S has coordinated to one metal center while the N was coordinated to a different metal, both S and N donor atoms have coordinated to the same metal ion as a straightforward chelating ligand, and the sulfur donor has functioned as a terminal thiolate ligand with only weak interactions between the nitrogen atom and the metal center.[5]

Relatively little is known about pyridineselenolate and pyridinetellurolate complexes, but given the recent descriptions of pyridineselenolate compounds of Li,[6] Cd, and Hg,[1a] it is already clear that compounds of the heavier chalcogens will be just as structurally diverse as are their sulfur analogs. More importantly, the pyridineselenolate ligand has been shown to useful in the synthesis of volatile compounds: pyridineselenolate complexes of Cd and Hg sublime intact and decompose at elevated temperatures to give CdSe and HgSe, respectively. In this paper, we extend pyridineselenolate chemistry to the main group elements Sn and Pb. The stability of both divalent and tetravalent oxidation states for these metal selenolates are determined, and potential use of these molecules as CVD sources of MSe or MSe$_2$ is illustrated. The 3-Me$_3$Si-2-SeNC$_5$H$_3$ ligand has also been prepared and used to make a crystalline lead(II) pyridineselenolate.

(5) (a) Umakoshi, K.; Kinoshita, I.; Ichimura, A.; Ooi, S. *Inorg. Chem.* **1987**, *26*, 3551−6. (b) Baghlaf, A. O.; Ishaq, M.; Rashed, A. K. A. *Polyhedron* **1987**, *6*, 837−9. (c) Brandenberg, K. L.; Heeg, M. J.; Abrahamson, H. B. *Inorg. Chem.* **1987**, *26*, 1064−9. (d) Umakoshi, K.; Kinoshita, I.; Ooi, S. *Inorg. Chim. Acta* **1987**, *127*, L41−2. (e) Rosenfield, S. G.; Berends, H. P.; Gelmini, L.; Stephan, D. W.; Mascharak, P. K. *Inorg. Chem.* **1987**, *26*, 2792−7. (f) Deeming, A. J.; Hardcastle, K. I.; Meah, M. N.; Bates, P. A.; Dawes, H. M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1988**, 227−33. (g) Deeming, A. J.; Meah, M. N.; Bates, P.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1988**, 2193−9. (h) Kumar, R.; de Mel, V.; Oliver, J. P. *Organometallics* **1989**, *8*, 2488−90. (i) Wang, S.; Fackler, J. P. *Inorg. Chem.* **1989**, *28*, 2616−29. (j) Ainscough, E. W.; Baker, E. N.; Bingham, A. G.; Brodie, A. W.; Smith, C. A. *J. Chem. Soc., Dalton Trans.* **1989**, 2167−71. (k) Ciriano, M. A.; Viguri, F.; Perez-Torrente, J. J.; Lahoz, F. J.; Oro, L. A.; Tiripicchio, A.; Camellini, M. *J. Chem. Soc., Dalton Trans.* **1989**, 25−32. (l) Umakoshi, K.; Kinoshita, I.; Fukui,-Yasuba, Y.; Matsumoto, K.; Ooi, S.; Nakai, H.; Shiro, M. *J. Chem. Soc., Dalton Trans.* **1989**, 815−9. (m) Kita, M.; Yamanari, K.; Shimura, Y. *Bull Chem. Soc. Jpn.* **1989**, *62*, 3081−8. (n) Castano, M. V.; Macias, A.; Castineiras, A.; Gonzalez, A. S.; Martinez, E. G.; Casas, J. S.; Sordo, J.; Hiller, W.; Castellano, E. E. *J. Chem. Soc., Dalton Trans.* **1990**, 1001−5. (o) Deeming, A. J.; Meah, M. N.; Randel, N. P.; Hardcastle, K. I. *J. Chem. Soc., Dalton Trans.* **1990**, 2211−6. (p) Deeming, A. J.; Karim, M.; Powell, N. I. *J. Chem. Soc., Dalton Trans.* **1990**, 2321−4. (q) Castro, R.; Duran, M. L.; Garcia-Vasquez, J. A.; Romero, J.; Sousa, A.; Castinerias, A.; Hiller, W.; Strahle, J. *J. Chem. Soc., Dalton Trans* **1990**, 531−4. (r) Yamamoto, J. H.; Yoshida, W.; Jensen, C. M. *Inorg. Chem.* **1991**, *30*, 1353−7. (s) Berardini, M.; Brennan, J. G. *Inorg. Chem.* **1995**, *34*, 6179.
(6) Khasnis, D.; Buretea, M.; Emge, T.; Brennan, J. *J. Chem. Soc., Dalton Trans.* **1995**, 45.

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. Anhydrous TMEDA and Me$_3$SiCl were purchased from Aldrich. Sn, Pb, Pb(OAc)$_4$, SnCl$_2$, and PbCl$_2$ 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 Kα 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 (in ppm) were recorded on a Varian XL 200 MHz NMR at 24.5 °C. Elemental analyses were performed by Quantitative Technologies, Inc. (Salem, NJ). Pyridineselenol was prepared as described previously.[1a]

Synthesis of [Sn(2-SeNC$_5$H$_4$)$_2$]$_2$ (1). Method A. Pyridine-2-selenol (3.5 g, 22.2 mmol) was dissolved in THF (100 mL) to give an orange solution. After the solution was cooled in an ice−water bath, NaB-(C$_2$H$_5$)$_3$H (22.3 mL of a 1 M solution in THF, 22.3 mmol) was added, and the solution turned pale yellow within 2 h. The solvent was removed under vacuum to give a pale-yellow powder (NaSePy) that was washed with diethyl ether. The powder was then added to a solution of SnCl$_2$ (2.1 g, 11.1 mmol) in THF (200 mL), and the mixture was stirred at room temperature for 1 day, as a brown solution color developed. The solution was filtered, concentrated (75 mL), and layered with hexane (50 mL) to give yellow crystals (1.27 g, 26.4%; mp 114.6 °C).

Method B. Sn powder (0.5 g, 4.2 mmol) was mixed with dipyridyl diselenide (1.0 g, 3.2 mmol) in toluene (10 mL), and the mixture was then refluxed for 12 h. The toluene was removed by vacuum to give a yellow powder that was first washed with diethyl ether (5 × 20 mL) and then dissolved in THF (50 mL). Filtration, followed by saturation of the solution with a layer of hexane, gave yellow crystals (0.86 g, 62%) that were identical to the material isolated by method A. Anal. Calcd for SnC$_{10}$H$_8$N$_2$Se$_2$: C, 27.6; H, 1.86; N, 6.47. Found: C, 27.6; H, 1.79; N, 6.36. ^{1}H NMR (CD$_3$COCD$_3$): 8.28 (1H, d ($J = 5$ Hz)), 7.55 (1H, m), 7.34 (1H, d ($J = 8$ Hz), 7.16 (1H, t ($J = 6$ Hz)). The compound sublimes without decomposition at 107 °C. EIMS: *m/e* 435.8 (M$^+$). IR (KBr): 1575 (s), 1545 (s), 1474 (w), 1441 (s), 1410 (s), 1262 (s), 1235 (w), 1142 (m), 1113 (s), 1074 (m), 1045 (m), 1007 (s), 988 (m), 872 (w), 803 (m), 766 (s), 751 (s), 730 (w), 697 (s), 639 (m), 624 (m) cm^{-1}.

Synthesis of Sn(2-SeNC$_5$H$_4$)$_4$ (2). Dipyridyl diselenide (0.50 g, 1.59 mmol) and Sn (0.095 g, 0.80 mmol) were mixed in toluene (10 mL). The mixture was stirred in the dark for 20 h at 70 °C to give a yellow precipitate that was collected and washed with diethyl ether (50 mL). The product was redissolved in hot pyridine, the solution was filtered, and the pyridine was removed under vacuum to give a yellow powder (0.46 g, 77%; mp 146−148 °C; dec ca. 250 °C). The product sublimes without decomposition at 142 °C (0.1 mmHg). Anal. Calcd for C$_{20}$H$_{16}$N$_4$Se$_4$Sn: C, 32.2; H, 2.16; N, 7.50. Found: C, 31.9; H, 2.10; N, 7.30. ^{1}H NMR (DMSO): 8.11 (1H, d ($J = 5$ Hz)), 7.60 (1H, m), 7.51 (1H, m), 7.17 (1H, t ($J = 5$ Hz)). IR (KBr): 1574 (s), 1562 (s), 1555 (s), 1468 (w), 1435 (s), 1417 (s), 1358 (m), 1272 (w), 1257 (s), 1241 (m), 1149 (s), 1119 (s), 1102 (s), 1077 (s), 1036 (s), 1005 (s), 985 (s), 957 (w), 883 (w), 873 (w), 767 (s), 750 (s), 724 (m), 696 (s), 641 (s), 616 (m), 468 (s), 415 (s), 405 (s) cm^{-1}.

Synthesis of Pb(2-SeNC$_5$H$_4$)$_2$ (3). Method A. NaSeNC$_5$H$_4$ (0.64 g, 3.55 mmol), prepared as above, was mixed with PbCl$_2$ (0.494 g, 1.78 mmol) in THF (100 mL), and a green precipitate formed instantly. After 1 day, the solvent was removed under vacuum, and the resultant green powder was washed with MeOH (100 mL) and then water (100 mL) to give a yellow-green powder (0.68 g, 63%).

Method B. Pb (0.50 g, 2.41 mmol) was added to dipyridyl diselenide (0.76 g, 2.42 mmol) in toluene (10 mL) and the mixture

was refluxed for 12 h. The solvent was removed by vacuum, and the remaining powder was washed with diethyl ether (5 × 20 mL) and cold pyridine (5 × 20 mL). The product was then dissolved in hot pyridine, and the mixture was filtered and dried in vacuum to give a yellow-green powder (1.1 g, 88%; mp 230−232 °C dec). Anal. Calcd for $C_{10}H_8N_2PbSe_2$: C, 23.0; H, 1.54; N, 5.37. Found: C, 22.6; H, 1.40; N, 5.01. The compound sublimes without decomposition at 188 °C (0.1 mm Hg). EIMS: m/e 523.9 (M^+). ^1H NMR (DMSO): 8.34 (1H, d (J = 4.4 Hz)), 7.41 (1H, t (J = 6.8 Hz)), 7.11 (2H, m). IR (KBr): 1570 (s), 1546 (m), 1440 (s), 1407 (s), 1263 (m), 1228 (w), 1144 (m), 1108 (s), 1071 (m), 1040 (m), 990 (s), 755 (s), 738 (s), 697 (s), 625 (s), 471 (s), 421 (w), 405 (m) cm^{-1}.

Attempted Synthesis of Pb(2-SeNC₅H₄)₄. NaSePy (1.13 g, 6.33 mmol) and lead(IV) tetraacetate (0.70 g, 1.58 mmol) were dissolved in THF (50 mL), and the mixture was stirred for 12 h at room temperature. The solution was filtered, and the precipitate was washed with THF, MeOH, and H_2O (5 × 30 mL each) to give yellow Pb-(SePy)₂ (0.5 g, 84%) and PySeSePy (0.41 g, 82%), which were identified by melting point and ^1H NMR spectroscopy. The organic product of the reaction was identified as dipyridyl diselenide by passing the filtrate through a silica column before analysis by GCMS.

Synthesis of Bis(3-(trimethylsilyl)-2-pyridyl) Diselenide (4). A mixture of tetramethylethylenediamine (7 mL, 46.4 mmol) and pyridine-2-selenol (2.87 g, 18.2 mmol) in hexane (30 mL) was cooled to −78 °C and then treated dropwise with n-butyllithium (15.9 mL of a 2.5 M solution in hexane, 39.8 mmol)) in hexane. The temperature was kept constant for an hour, and then raised to room temperature over a 3 h period. The solution, which turned homogeneous, was stirred at room temperature for 12 h, and an off-white solid formed. The mixture was cooled to −78 °C, and Me₃SiCl (5.06 mL, 39.8 mmol) in THF (15 mL) was added slowly. After being stirred at room temperature for 12 h, the mixture was taken to dryness under vacuum. A solution of acetic acid (5 mL) in water (2 L) was added to the solid, and the product was extracted with CH_2Cl_2 (3 × 50 mL). The CH_2Cl_2 extract was dried over $MgSO_4$, and the solution was filtered and concentrated in vacuo to give a yellow powder that was washed repeatedly with petroleum ether to give yellow **4** (1.9 g, 45%; m.p. 202−4 °C). Anal. Calcd for $C_8H_{12}NSeSi$: C, 41.9; H, 5.28; N, 6.11. Found: C, 41.3; H, 5.59; N, 5.97. EIMS: 460.0 (M^+). ^1H NMR (CDCl₃): 8.20 (1H, b), 7.59 (1H, d of d (J = 7 Hz, 2 Hz)), 7.00 (1H, broad t (J = 6 Hz)). IR (KBr): 3132 (m), 3100 (m), 3071 (m), 3036 (s), 2965 (s), 2919 (s), 2892 (s), 2849 (s), 2757 (m), 2675 (w), 1909 (w), 1834 (w), 1775 (w), 1600 (s), 1571 (s), 1545 (m), 1478 (w), 1428 (w), 1356 (m), 1303 (s), 1245 (m), 1235 (m), 1202 (m), 1120 (s), 1061 (m), 1036 (m), 1004 (w), 948 (w), 897 (w), 848 (s), 749 (s), 714 (w), 697 (m), 645 (m), 622 (m), 416 (m) cm^{-1}.

Synthesis of Pb(3-Me₃Si-2-SeNC₅H₃)₂ (5). A solution of NaB-(C₂H₅)₃H in THF (4.42 mL of a 1M solution, 4.42 mmol) was added to bis[3-(trimethylsilyl)-2-pyridine] diselenide (1.0 g, 2.2 mmol) in THF (30 mL). After stirring the solution for 2 h at room temperature, the solvent was removed under vacuum, and the resulting pale yellow solid was washed with diethyl ether (100 mL). The product was redissolved in THF (30 mL), and PbCl₂ (0.824 g, 2.96 mmol) was added. After a day, the solution was filtered and the THF was removed by slow evaporation to give yellow crystals (0.76 g, 38.6%; mp 212−214 °C) that were collected and washed with cold hexane. Anal. Calcd for PbC₁₆H₂₄N₂Se₂Si₂: C, 28.9; H, 3.63; N, 4.21. Found: C, 28.8; H, 3.36; N, 4.20. The compound sublimes at 190 °C (0.1 mmHg) without decomposing. EIMS: m/e 668.0 (M^+). ^1H NMR (CDCl₃): 8.41 (1H, d of d (J = 4.8 and 1.8 Hz)), 7.60 (1H, d of d (J = 7.3 and 1.8 Hz)), 7.04 (1H, d of d (J = 7.3 and 4.8 Hz)), 0.41 (9H, s). IR (KBr): 3094 (m), 3026 (s), 2950 (s), 2892 (s), 1928 (m), 1903 (w), 1752 (w), 1726 (w), 1549 (s), 1443 (w), 1407 (m), 1354 (s), 1245 (s), 1223 (m), 1200 (m), 1119 (s), 1057 (s), 966 (w), 942 (w), 841 (s), 786 (m), 754 (s), 687 (s), 650 (s), 622 (s), 497 (m), 439 (m) cm^{-1}. Unit cell obtained on a potentially twinned crystal (Mo Kα, room temperature): a, 23.798-(2) Å; b, 14.447(3) Å; c, 20.396(3) Å; $\alpha = \beta = \gamma = 90°$ ($Cmc2_1$).

Thermolysis of 1, 2, and 3. Samples were placed in Pyrex tubes which were then sealed under vacuum and then heated to ca. 300 °C. Initially, the entire sample container was heated to decompose the sample, and then one end of the tube was placed outside the oven in

Table 1. Crystal Data and Structure Refinement for **1**

empirical formula	$C_{10}H_8N_2Se_2Sn$	Z	8
fw	432.79	D(calcd) (Mg/m³)	2.259
space group	*Pbca*	T (K)	293
a (Å)	8.214(1)	λ (Å)	0.710 73
b (Å)	21.181(3)	abs coeff (mm⁻¹)	7.7
c (Å)	14.628(2)	no. of obsd reflcns	930
α (deg)	90.0	$R(F)^a$ [I > 2σ]	0.058
β (deg)	90.0	$R_w(F^2)^a$ indices	0.053
γ (deg)	90.0	[I > 2σ]	
V (Å³)	2545.0(6)		

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

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

Sn−N1′	2.320(8)	Sn−Se2	2.681(2)
Sn−N2	2.717(12)	Sn−Se1	2.759(1)
Sn−Se1′	3.320(1)	Sn−Se2″	3.618(2)
Se1−C1	1.888(11)	Se2−C6	1.88(2)
N1−Sn′	2.320(8)		

N1′−Sn−Se2	93.2(2)	N1′−Sn−N2	76.3(3)
Se2−Sn−N2	60.7(3)	N1′−Sn−Se1	86.0(3)
Se2−Sn−Se1	86.72(4)	N2−Sn−Se1	141.3(3)
N1′−Sn−Se1′	55.8(2)	Se2−Sn−Se1′	147.03(5)
N2−Sn−Se1′	114.6(2)	Se1−Sn−Se1′	80.80(3)
N1′−Sn−Se2″	171.4(2)	Se2−Sn−Se2″	79.88(2)
N2−Sn−Se2″	104.3(2)	Se1−Sn−Se2″	88.43(5)
Se1′−Sn−Se2″	129.70(5)	C1−Se1−Sn	97.1(3)
C6−Se2−Sn	85.7(5)		

order to condense the volatile products. In the thermolysis of **1** and **3** an X-ray powder diffraction profile of the resultant gray-black microcrystalline solid indicated that MSe was the only crystalline phase present. Py−Se−Py was identified as the major organic thermolysis product by GCMS and ^1H NMR spectroscopy (as the thermolysis temperature was increased, increasing amounts of pyridine and bipyridine were observed). Yields of solid state materials were essentially quantitative. The lead compounds showed a tendency to reductively eliminate PySeSePy at low (260 °C) temperatures (ca. 1:10 PySeSePy: PySePy, by ^1H NMR integration), but above 450 °C any eliminated PySeSePy is apparently consumed, and only PbSe/py/PySPy were observed. Both PySePy and PySeSePy decompose to give elemental Se and pyridine. Trace amounts of Se crystals were deposited near the oven aperture during the thermolyses at elevated temperatures (500 °C), and a significant quantity of Se deposited during the thermolysis of **2** at 500 °C. At 300 °C, **2** decomposed to give quantitative yields of SnSe₂ and PySePy.

X-ray Crystallography of 1. Data for **1** were collected on a CAD4 diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.710 73 Å) at room temperature. The 3 check reflections measured every 3 h showed less than 2% intensity variation. The data were corrected for Lorenz effects and polarization, and absorption, the latter by a numerical (SHELX76)[7a] method. The structure was solved by Patterson methods (SHELXS86).[7b] All non-hydrogen atoms were refined (SHELXL93)[8] based upon F_{obs}. All hydrogen atom coordinates were calculated with idealized geometries (SHELXL93). Crystallographic data and final R indices for **1** are given in Table 1. Significant bond distances and angles for **1** are given in Table 2. Complete crystallographic details are given in the supplemental material.

Results and Discussion

Synthesis and Structure. The pyridineselenolate complex of Sn(II) can be prepared either by metathesis (reaction 1), or by the reduction of dipyridyl diselenide with elemental Sn in

(7) (a) Sheldrick, G. M. SHELX76 Program for Crystal Structure Determination, University of Cambridge, England, 1976. (b) Sheldrick, G. M. SHELXS86, Program for the Solution of Crystal Structures, University of Gottingen, Germany, 1986.

(8) Sheldrick, G. M. SHELXL-93, Program for Crystal Structure Refinement, University of Gottingen, Germany, 1993.
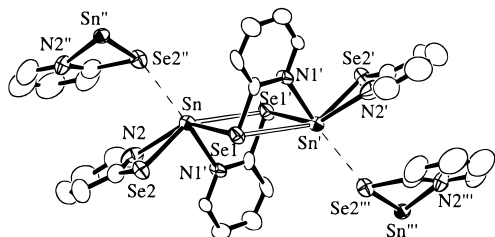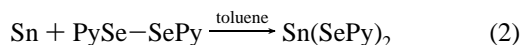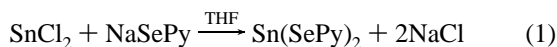
Figure 1. Molecular structure of [Sn(2-SeNC$_5$H$_4$)]$_2$. The dimeric compound has Sn(II) ions in distorted octahedral geometries, with two strong Sn−Se bonds (Sn−Se1 = 2.759(1) Å; Sn−Se2 = 2.681(2) Å), two weak (Sn−Se1′ = 3.320(1) Å; Sn−Se2″ = 3.618(2) Å) Sn−Se interactions, and two Sn−N bonds (Sn−N1′, 2.320(8) Å; Sn−N2, 2.717(12) Å).

refluxing toluene (reaction 2). Both reactions give a yellow

$$SnCl_2 + NaSePy \xrightarrow{THF} Sn(SePy)_2 + 2NaCl \qquad (1)$$

$$Sn + PySe-SePy \xrightarrow{toluene} Sn(SePy)_2 \qquad (2)$$

solid that can be crystallized from THF. The product is soluble in toluene, pyridine, acetone, and THF and insoluble in noncoordinating solvents such as hexane. An ^{1}H NMR analysis of the compound indicated only the presence of a single type of pyridineselenolate ligand environment, and the mass spectrum showed only that the compound was monomeric in the gas phase. For unambiguous structural assignment, the product was studied by single-crystal X-ray diffraction, and shown to be dimeric [Sn(2-SeNC$_5$H$_4$)$_2$]$_2$ (**1**). Table 2 gives a listing of significant bond lengths and angles for **1**, and Figure 1 shows an ORTEP diagram of the compound. The structure of **1** contains a number of interesting features. First, there are two different metal-ligand bonding modes: one chelating N,Se bound pyridineselenolate (Sn−Se2, 2.681(2) Å; Sn−N2, 2.717-(2) Å), and one ligand that asymmetrically spans two metal centers, with the N bound to one metal (Sn−N, 2.320(8) Å) and the Se bound to the other (Sn−Se1, 2.759(1) Å). The differences between Sn−N distances illustrate how optimal orientation of the nitrogen donor strengthens the Sn−N bond. Second, there are a number of weak Sn−Se interactions; i.e. between Sn and Se1′ (Sn−Se1′, 3.320(1) Å) and between Sn and Se2″ (Sn−Se2″, 3.618(2) Å). If the later is viewed as a significant interaction, then the compound can alternatively be formulated as a polymer. In the gas phase all weak interactions are absent, and the compound sublimes as a monomer.

The structure of **1** resembles the structure of SnSe in terms of coordination geometry and the number of weak/strong bonding interactions. SnSe is described as a distorted NaCl structure,[9] with three strong Sn−Se bonds (2.77, 2.82, and 2.82 Å) and three weak Sn−Se interactions (3.35, 3.35, and 3.47 Å). Molecular **1** also has three strong bonding interactions (Sn−Se1, 2.76 Å; Sn−Se2, 2.68 Å; Sn−N1′, 2.32 Å) and three that are relatively weak (Sn−N2, 2.72 Å; Sn−Se1′, 3.32 Å; Sn−Se2″, 3.62 Å). Bond angles in **1** and SnSe are not comparable because the chelating ligand imposes geometric constraints that are absent in SnSe.

The bridging selenolate geometry in **1** represents a new bonding mode for the pyridineselenolate ligand. The BIPY coordination complex of Li-2-SeNC$_5$H$_4$ was also dimeric in the solid state,[6] with the N and Se of each ligand coordinating to different Li ions to form an 8-membered ring. However, the bonding in **1** differs from the Li structure because of the weak

Sn−Se1′ interaction that has no parallel in the tetrahedral Li structure. There are also bridging pyridineselenolate ligands in polymeric Cd(SePy)$_2$,[1a] in which bridging pairs of selenium atoms spanned adjacent metal ions and the corresponding nitrogen donors were bound to different metals. The bridging interaction in **1** also differs from that in the Cd structure, where the Cd−Se bonds were all roughly equivalent.

Bonding between Sn and the chelating pyridineselenolate ligand in **1** is also different from the ligation in Hg(SePy)$_2$. The Hg and Sn structures both contain chelating ligands which have weak intermolecular M−Se interactions, but there is a differences in the degree of relative bonding to the heteroatoms. In the Hg compound, the Hg−N (2.984(1) Å) and Hg−Se (2.458-(1) Å) bond lengths indicate that the Hg−N interaction is considerably weaker than the Sn−N interaction found in **1**.

The reported synthesis of Sn(SePh)$_4$[10] left little doubt that the resonance stabilized pyridineselenolate ligand would also stabilize Sn(IV). Sn(SePy)$_4$ can be prepared either by the oxidation of **1** with PySeSePy, or in a one step reaction by reducing 2 equiv of the diselenide with elemental Sn. Either method gives the yellow tetrapyridineselenolate compound Sn-(SePy)$_4$ (**2**) in ca. 70% yield. This compound is soluble in pyridine and THF and slightly soluble in toluene. As found for **1**, the Sn(IV) compound has averaged pyridineselenolate resonances in the ^{1}H NMR spectrum. X-ray quality crystals of this compound were not isolated, and so it is impossible to unambiguously assign a structure to the molecule. In related thiolate work, a structural determination of analogous Sn(SPy)$_4$ complex[11] (which crystallized with an equivalent of HSPy in the lattice) showed an octahedral metal center having two monodentate and two bidentate pyridinethiolate ligands (that were equivalent on the NMR timescale), while the structure of Sn(3-Me$_3$Si-2-SPy)$_4$ contained an 8-coordinate Sn(IV) ion with four equivalent chelating ligands.[12a]

The pyridineselenolate chemistry of Pb is more limited, due to the relative instability of the Pb(IV) oxidation state. As found for tin, divalent Pb(SePy)$_2$ (**3**) can be prepared either by metathesis or by insertion of Pb into the Se−Se bond of PySeSePy. In contrast to **1**, the divalent Pb complex is air stable. The absence of further reaction of the Pb(II) compound with dipyridyl diselenide was the first indication that pyridineselenolate would not effectively stabilize Pb(IV). This was confirmed by approaching the synthesis of Pb(SePy)$_4$ from tetravalent Pb starting materials: the reaction of Pb(OAc)$_4$ with 4 equiv of NaSePy in THF also resulted in the formation of Pb(SePy)$_2$ (eq 3). The organic product of the reductive

$$PbCl_2 + 2NaSePy \rightarrow Pb(SePy)_2 \leftarrow Pb(OAc)_4 + 4NaSePy \qquad (3)$$
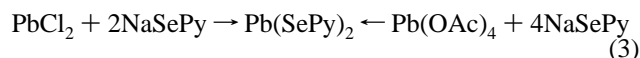
elimination, dipyridyl diselenide, can be isolated in near quantitative yield. The tendency of metals in higher oxidation states to reductively eliminate dichalcogenides has been noted in redox active lanthanide chalcogenolate systems.[13] The isolation of **3** and PySeSePy from tetravalent Pb starting materials is conclusive evidence for the instability of Pb(SePy)$_4$. Because the compound is relatively insoluble (dissolving only

(9) (a) Okazaki, A.; Ueda, I. *J. Phys. Soc. Jpn.* **1956**, *11*, 470. (b) Wiedemeier, H.; von Schnering, H. G. *Z. Kristallorg.* **1978**, *148*, 295.

(10) Rajesh, K.; Hassan, E.; Mabrouk, H. E.; Tuck, D. *J. Chem. Soc., Dalton Trans.* **1988**, 1045.

(11) Damude, L.; Dean, P.; Manivannan, V.; Srivastava, R. S.; Vittal, J. J. *Can. J. Chem.* **1990**, *68*, 1323.

(12) (a) Block, E.; Ofori-Okai, G. Kang. H.; Wu, J.; Zubieta, J. *Inorg. Chim. Acta* **1991**, *190*, 5. (b) Block, E.; Gernon, M.; Kang, H.; Ofori-Okai, G.; Zubieta, J. *Inorg. Chem.* **1991**, *30*, 1736. (c) Block, E.; Ofori-Okai, G.; Chen Q.; Zubieta, J. *Inorg. Chim. Acta* **1991**, *189*, 137.

(13) (a) Berardini, M.; Emge, T.; Brennan, J. G. *J. Am. Chem. Soc.* **1993**, *115*, 8501. (b) Khasnis, D.; Lee, J.; Brewer, M.; Emge, T. J.; Brennan, J. G. *J. Am. Chem. Soc.* **1994**, *116*, 7129.

in hot pyridine or DMSO, but not acetone, THF, or toluene) and has a melting point 120 °C higher than the analogous Sn compound **1**, we conclude that **3** is polymeric in the solid state.

The poor solubility of complex **3** made purification difficult, and so the solubility of the lead selenolate was increased by replacing H with a Me_3Si group at the 3-position of the pyridineselenolate ring. Inspiration for this substitution came from the related pyridinethiolate chemistry of Block *et al.*,[12] in which introduction of a bulky substituent has been shown to modify the tendency of thiolates to bridge the metal sites and/ or decrease the associated lattice energy of crystalline material, thus enhancing complex solubility. Block's convenient and readily reproduced preparation of the $3\text{-}Me_3Si\text{-}2\text{-}SNC_5H_3$ ligand from the reaction of pyridinethiol/lithium diisopropylamide and Me_3SiCl could not be extended directly to selenolate chemistry, but instead pyridineselenol can be lithiated at the 3-position with *n*-butyllithium,[14] and the reaction of the 3-lithiated selenolate with Me_3SiCl gave the desired product in 45% yield. The corresponding Pb(II) derivative was prepared by reacting the trimethylsilylated diselenide with elemental Pb in refluxing toluene, and crystallizing from THF. This compound has a unit cell that is almost identical to the analogous thiolate derivative (a trimeric compound containing Pb(II) ions in trigonal bipyramidal and square pyramidal geometries), but twinning prevented a complete X-ray diffraction analysis of the product. It is interesting to note that while this substituent had the desired effect in terms of enhancing solubility properties, it did not lead to a significant change in either melting or sublimation point.

Thermolysis. Thermal decomposition of metal chalcogenolates to give metal chalcogenide solids is a well-established process that dates back to early German work on metal thiolate decompositions.[15] Generally, divalent chalcogenolates decompose to give ME, and trivalent molecules decompose to give M_2E_3. The predominant organic byproducts are R_2E, where R can be aryl, alkyl, or silyl and E can be any of the chalcogens. Exceptions to this rule generally occur when the target solid state phase is thermodynamically unstable, as in the thermal decomposition of $[PEt_4][Eu(SPy)_4]$ to give EuS,[5s] rather than Eu_2S_3, when the precursor has a particularly stable cluster structure,[1s] or when reductive elimination of R_2E_2 is favored, as in the decomposition of some mercury chalcogenolate precursors.

It is clear from early work in group IV metal chemistry that metal chalcogenolate thermolysis results in the formation of metal chalcogenide solids; both aromatic and halogenated aromatic lead thiolates were found to yield PbS upon decomposition.[1q] Silylated chalcogenolates were recently shown to give ME (M = Sn, Pb; E = S, Se, Te) contaminated by elemental M;[1b] this reactivity parallels the chemistry of Pb-$(SBu)_2$,[1aa] although in the latter case the formation of elemental Pb was supressed at elevated temperatures. There are also reports of $[Ph_2SnSe]_3$ decomposing to give SnSe.[16]

In the present system, the thermolysis of **1** gave SnSe, and the thermolysis of **3** gave PbSe.[17] Both solid state products were identified by their characteristic X-ray powder diffraction profiles. The yields are quantitative, and the primary volatile organic product observed was Py—Se—Py. Both elemental Se

and pyridine can also be detected in increasing amounts as the pyrolysis temperature is increased.[18] These thermolyses were actually problematic under our usual thermolysis conditions in which part of the tube is held outside the oven to condense the organic products, because the molecules are so volatile that they had a tendency to sublime into the cold part of the thermolysis tube. When we first heated the entire sample container in the oven and then placed one end of the tube at room temperature, essentially quantitative yields of MSe were obtained.

The low temperature synthesis of solid state $SnSe_2$ from volatile **2** is complicated because $SnSe_2$ sublimes intact[19] and decomposes at elevated temperatures/reduced pressure to give SnSe and Se.[20] For these reasons, the thermolysis of the Sn-(IV) compound **2** had to be studied at relatively low temperatures. At 300 °C, the only volatile product in the thermal decomposition of **2** was PySePy. The absence of elemental Se suggested that reductive elimination was not occuring, and this was confirmed when the X-ray powder diffraction profile showed that $SnSe_2$ was the only crystalline phase present.[21] The synthesis of both SnSe and $SnSe_2$ from **1** and **2** may be particularly useful in controling the M:Se ratios of MSe thin films.

Conclusions

The pyridineselenolate ligand forms stable homoleptic complexes with Sn(II), Sn(IV), and Pb(II). Structural characterization of $Sn(SePy)_2$ complex showed the complex to be dimeric in the solid state, with one chelating ligand and one ligand that asymmetrically spans the two Sn(II) centers. From the Sn—N distances, it is clear that interaction between the Sn ion and the chelating SePy nitrogen is considerably stronger than the related M—N interactions in $Hg(SePy)_2$, and thus this structure contains two new bonding modes for the pyridineselenolate ligand. A trimethylsilyl substituent at the 3-position of the pyridine ring increases the solubility of the Pb(II) complex and permits the isolation of crystalline material.

The divalent compounds sublime and can be used for the vapor phase deposition of MSe (M = Sn, Pb). According to mass spectroscopy, the compounds are all monomeric in the gas phase. The Sn(IV) complex also sublimes intact and decomposes to give $SnSe_2$.

Supporting Information Available: X-ray powder diffraction patterns of thermolysis products of **1**–**3**, mass spectra for **1**, **2**, **4**, and **5**, and tables of crystallographic details and refinement results complete atomic parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom parameters for **1** (23 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(14) Collum, D. B. *Acc. Chem. Res*. **1992**, *25*, 448.
(15) Otto, R. *Chem. Ber.* **1880**, *13*, 1289.
(16) (a) Boudjouk, P.; Seidler, D. J.; Bahr, S. R.; McCarthy, G. J. *Chem. Mater.* **1994**, *6*, 2108. (b) Bahr, S.; Boudjouk, P.; McCarthey, G. J. *Chem. Mater.* **1992**, *4*, 383.
(17) Halla, F.; Mehl, E.; Bosch, F. X. *Z. Phys. Chem.* **1931**, *B12*, 377.

(18) Keats, N. G.; Summers, L. A. *J. Heterocycl. Chem.* **1979**, *16*, 1369.
(19) Busch, G.; Frohlich, C.; Hulliger, F.; Steigmeier, E.; *Helv. Phys. Acta* **1961**, *34*, 359.
(20) Novoselova, A. V.; Zlomanov, V. P.; Karbanov, S. G.; Matveyev, O. V.; Gaskov, A. M.; *Prog. Solid State* **1972**, *7*, 85.
(21) Palatnik, L. S.; Levitin, V. V. *Doklady Akad. Nauk. S.S.S.R.* **1954**, *96*, 975.