Synthesis and Structure of Telluroamides and Selenoamides. The First Crystallographic Study of Telluroamides

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The reaction between bis(trialkyltin) chalcogenides and trimethylaluminum results in the formation of bis(dimethylaluminum) chalcogenides, $(Me_2Al)_2E$, where E is S, Se, or Te. Reaction between the latter and carbonyl groups (but not carboxylic acids or esters) converts them to carbon−chalcogen double-bond (C═E) compounds. Using this procedure, we have successfully synthesized several telluro- and selenocarbonyl compounds. The first successful synthesis of an isolable, crystalline telluroformamide, 4-(telluroformyl)morpholine (**3c**, C_5H_9NOTe), and its crystal structure are reported. Also, the syntheses and crystal structures of a γ-tellurolactam, 1-methyl-2-telluroxopyrroline (**3d**, C_5H_9NTe), and two selenoamides, *N*,*N*-diphenylselenoformamide (**3a**, $C_{13}H_{11}NSe$) and *N*-methyl-*N*-(4-nitrophenyl) selenoformamide (**3b**, $C_8H_8N_2O_2Se$) are described.

Introduction

The reaction between thio- or selenocarbonyls and complexed metal ions in homogeneous solution has served for the preparation, by chemical deposition, of semiconducting thin films of metal chalcogenides. Typical examples are the preparation of ZnSe and CuSe by the reaction of complexed zinc and copper with *N*,*N*-dimethylselenourea to yield films of ZnSe and CuSe[1] and similar reactions which utilize thioacetamide for the chemical deposition of ZnS, PbS, and CuS.[2]

Because of the great potential of CdTe as a semiconducting material, we have attemped the preparation of tellurocarbonyls, which could be useful in the manner described for thio- and selenocarbonyls.

In recent years, the chemistry of carbon−selenium and carbon-tellurium double-bonded compounds such as seleno- and telluroaldehydes and seleno- and telluroketones, which are generally unstable, has been actively studied.[3] Seleno- and telluroamides and seleno- and telluroesters, due to the resonance effect of nitrogen or oxygen,[4] have been considered to be more stable than seleno- and telluroaldehydes (or ketones).[5] Actually, several selenoamides and selenoesters have been isolated.[6] However, since Barton and co-workers[7] prepared the first telluroesters in 1979, only a few additional tellurocarbonyl compounds have been isolated,[8] and no crystal structures of telluroamides or esters have been reported. Recently, we have reported that bis(dimethylaluminum) chalcogenides, $(Me_2Al)_2E$, where E is S, Se, or Te, displace the oxygen of a carbonyl to give the corresponding thio-, seleno- or tellurocarbonyl compound.[3p,q,6f,9] This procedure has been utilized later by Denifl and Bildstein to prepare diferrocenyl seleno- and telluroketones, $(Fc)_2C$═E, where E is Se or Te.[10] In this paper, we describe the syntheses and crystal structures of several new telluro- and selenoamides as well as some of their spectroscopic properties. To our knowledge, this is the first report on the crystal structures of telluroamides, although the structure of one tellurourea has been described.[8d]

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Experimental Section

General Considerations. Toluene, THF, and dioxane were carefully refluxed over potassium or sodium metal and distilled under argon prior to use. Reactions were carried out under an atmosphere of dry argon. When tellurium compounds were prepared, all glassware was wrapped in aluminum foil because of the characteristic photosensitivity of tellurium compounds. Laboratory lights were extinguished so as to minimize any illumination. All laboratory reagents were purchased from Aldrich Chemical Co. Selenium and tellurium powders were provided by the Selenium-Tellurium Development Association. The use of a very dry, air-free environment is essential for the success of these syntheses. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-200 NMR spectrometer (200.1 MHz for ^{1}H, 50.3 MHz for ^{13}C) using $CDCl_3$ as the solvent. The ^{1}H NMR chemical shifts were referenced to the residual proton line (δ 7.24 ppm) from $CDCl_3$ (99.8% D) and ^{13}C NMR chemical shifts to $CDCl_3$ (δ 77.0 ppm). ^{77}Se and ^{125}Te NMR spectra were measured in $CDCl_3$ solution with PhSeSePh (δ 460 ppm referenced to Me_2Se)[11a] or PhTeTePh (δ 420.8 ppm referenced to Me_2Te)[11b] as the external standards using a Varian XL-200 broad-band NMR spectrometer (38.2 MHz for ^{77}Se, 63.1 MHz for ^{125}Te), and the chemical shifts (ppm) have been converted relative to Me_2Se or Me_2Te. Mass spectra were run with a Hitachi M-80 instrument in the EI mode or a VG-70S spectrometer in the +FAB/DP mode. IR spectra were recorded on a Galaxy FT-IR 5000 spectrometer. UV−vis spectra were recorded on a Hitachi 200-10 spectrophotometer. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc.

Preparation of Bis(tributyltin) Selenide (1a) and Bis(trimethyltin) Telluride (1b). The procedure used was that described for the preparation of bis(trialkylsilyl) selenides or tellurides by Detty et al.,[12] except for the substitution of R_3SnCl for R_3SiCl. Bis(tributyltin) selenide, $(Bu_3Sn)_2Se$ (**1a**; bp 175−180 °C/0.5 mm; 15.13 g, 90%) was prepared by the reaction between 19.30 g (56.92 mmol) of Bu_3SnCl (assay 96%) and Li_2Se generated *in situ* from 2.00 g (25.33 mmol) of finely powdered Se and 55.0 mL of Super-Hydride (lithium triethylborohydride, 1 M in THF). ^{1}H NMR ($CDCl_3$; δ, ppm): 1.45−1.70 (m, 2H, $CH_3\mathbf{CH_2}CH_2CH_2$); 1.20−1.45 (m, 2H, $CH_3CH_2\mathbf{CH_2}CH_2$); 1.10 (t, J = 8.08 Hz, 2H, $CH_3CH_2CH_2\mathbf{CH_2}$); 0.89 (t, J = 7.20 Hz, 3H, $\mathbf{CH_3}CH_2CH_2CH_2$).

$(Me_3Sn)_2Te$ (**1b**; bp 72−75 °C/0.5 mmHg; 7.15 g, yield 80%) was obtained from 40 mL of Me_3SnCl (1 M in THF) and Li_2Te generated *in situ* from 2.50 g (19.6 mmol) of Te powder and 40.0 mL of Super-Hydride (lithium triethylborohydride, 1 M in THF). ^{1}H NMR ($CDCl_3$; δ, ppm): 0.56 (s).

Synthesis of *N*,*N*-Diphenylselenoformamide (3a). The same procedure described in a previous communication[6f] was used. Under a dry argon atmosphere, 1.60 g (2.43 mmol) of $(Bu_3Sn)_2Se$ (**1a**), toluene (15 mL), and Me_3Al (2 M toluene solution, 2.5 mL, 5 mmol) were stirred in a 50 mL three-necked, round-bottom flask at 40−50 °C for 4 h. This produces $(Me_2Al)_2Se$ (**2a**) in the form of a white suspension in toluene. The addition of THF (5 mL) converted the suspension to a clear solution. To the latter was added 550 mg (2.76 mmol) of *N*,*N*-diphenylformamide. The mixture was stirred at 40−50 °C for 5 h and then poured into ice−water (50 mL) and extracted with ethyl acetate (50 mL × 2). The organic extract was shaken with brine (100 mL). The phases were separated; the organic phase was dried over $MgSO_4$ and evaporated to give an orange oil. The oil was chromatographed through silica gel (60−200 mesh) with hexane−CH_2Cl_2 (4:1 → 2:1 → 1:1) as the solvent. Evaporation of the eluate gave 530 mg (yield 83%) of the selenoformamide (**3a**) in the form of yellow-orange crystals (mp 127.0−128.0 °C). Crystals for X-ray analysis were prepared by recrystallization from CH_2Cl_2 stored under refrigeration. Anal. Calcd for $C_{13}H_{11}NSe$: C, 60.01; H, 4.26; N, 5.38. Found C, 60.00; H, 4.28; N, 5.45. ^{1}H NMR ($CDCl_3$; δ, ppm): 11.74 (s, 1H, $Se{=}\mathbf{CH}N$); 7.15−7.65 (m, 10H, aromatic). ^{13}C NMR ($CDCl_3$; δ, ppm): 193.95 ($\mathbf{Se{=}C}HN$); 146.92, 142.58, 129.88, 129.72, 128.68, 127.52, 127.43, 122.34 (aromatic). ^{77}Se NMR ($CDCl_3$; δ, ppm): 793.4. Mass (+FAB/DP mode; *m/e*): 230 ($[M + H]^+$, ^{80}Se). IR (KBr; cm^{-1}): 3058, 2987, 1594, 1493, 1399, 1307, 1240, 999, 894, 762, 697, 618.

Synthesis of *N*-Methyl-*N*-(4-nitrophenyl)selenoformamide (3b). The starting formamide was prepared by formylation of methyl(4-nitrophenyl)amine with formic acid in acetic anhydride.[13] The mixture of formic acid (18 mL) and acetic anhydride (45 mL) was heated at 50−60 °C for 2 h and then cooled to 20−30 °C. With stirring, methyl(4-nitrophenyl)amine (32.0 g) was added in quantities just sufficient to maintain the internal temperature below 40 °C. The stirring was continued at 30−40 °C for 4 h. The reaction mixture was cooled over an ice−water bath, and ethyl acetate (150 mL) followed by water (200 mL) was added. The organic phase was separated, washed with water (300 mL × 3), and slowly evaporated to yield a pale yellow solid. The solid was washed with CH_2Cl_2−hexane (1:2) and then benzene and dried under reduced pressure. The light yellow solid, *N*-methyl-*N*-(4-nitrophenyl)formamide, was obtained in a yield of 60% (22.0 g; mp 119.0−121.0 °C, lit.[14a] 116 °C, lit.[14b] 118−120 °C). ^{1}H NMR ($CDCl_3$; δ, ppm): 8.70 (s, 1H, $O{=}\mathbf{CH}N$); 8.27 (dt, J = 9.20, 2.20 Hz, 2H, aromatic); 7.31 (dt, J = 9.20, 2.20 Hz, 2H, aromatic); 3.36 (s, 3H, $N\mathbf{CH_3}$).

To a white suspension of $(Me_2Al)_2Se$ (**2a**) in toluene (15 mL), generated from 1.60 g (2.43 mmol) of **1a** and 2.5 mL (5 mmol) of Me_3Al (2 M in toluene) as described above, was added THF (5 mL) followed by 500 mg (2.77 mmol) of *N*-methyl-*N*-(4-nitrophenyl)formamide. The mixture was stirred at 20−30 °C for 10 h[15] and then treated in the same manner described for

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3a. Selenoformamide **3b** was isolated in the form of orange crystals (mp 115.0−116.0 °C; 150 mg, yield 25.4%) by column chromatography on silica gel (60−200 mesh) with hexane-CH_2Cl_2 (4:1 → 2:1 → 1:1) as the solvent. Crystals for X-ray analysis were prepared by recrystallization from CH_2Cl_2 stored under refrigeration. Anal. Calcd for $C_8H_8N_2O_2Se$: C, 39.52; H, 3.32; N, 11.52. Found: C, 39.04; H, 3.52; N, 10.93. ^1H NMR ($CDCl_3$; δ, ppm): 11.60 (s, 1H, Se=**CH**N); 8.30 (dt, J = 9.20, 2.20 Hz, 2H, aromatic); 7.44 (dt, J = 9.20, 2.20 Hz, 2H, aromatic); 3.83 (s, 3H, N**CH₃**). ^{13}C NMR ($CDCl_3$; δ, ppm): 194.03 (**Se=C**HN); 151.11, 146.01, 125.52, 121.34 (aromatic); 41.16 (N**CH₃**). ^{77}Se NMR ($CDCl_3$; δ, ppm): 853.0. Mass (+FAB mode; *m/e*): 214 ($[M + H]^+$, ^{80}Se). IR (KBr; cm^{-1}): 1607, 1514, 1336, 1287, 1104, 1004, 847, 747, 687.

Synthesis of 4-(Telluroformyl)morpholine (3c). The synthesis of tellurocarbonyl compounds was carried out by following the procedure described for selenocarbonyls, with some modification. In an aluminum-foil-wrapped, very dry, and air-free 50 mL three-necked flask, 1.50 g (3.30 mmol) of $(Me_3Sn)_2Te$ (**1b**), toluene (15 mL), and Me_3Al (2 M toluene solution, 3.6 mL, 7.2 mmol) were stirred at 60−70 °C for 15 h under an argon atmosphere. This forms $(Me_2Al)_2Te$ (**2b**) as a white suspension. The addition of dioxane (5 mL) converted the suspension to a clear solution. To the latter was added 385 mg (3.31 mmol) of 4-formylmorpholine (assay 99%). The mixture (a deep purple solution) was stirred at 80−90 °C for 3 h, followed by evaporation. The residue (a dark purple oil) was purified by flash column chromatography on Florisil (60−100 mesh) with CH_2Cl_2 as the solvent. Evaporation of the eluate gave 520 mg (yield 69.5%) of 4-(telluroformyl)morpholine (**3c**) in the form of yellow-orange crystals (mp 84.0−86.0 °C dec). Crystals for X-ray analysis were prepared by dissolution in CH_2Cl_2 followed by slow evaporation. Anal. Calcd for C_5H_9NOTe: C, 26.49; H, 4.00; N, 6.18. Found: C, 22.71; H, 3.81; N, 5.52. ^1H NMR ($CDCl_3$; δ, ppm): 12.88 (s, 1H, Te=**CH**N); 4.17 (t, J = 4.96 Hz, 2H); 3.84 (t, J = 4.96 Hz, 2H); 3.75 (t, J = 4.89 Hz, 2H); 3.59 (t, J = 4.89 Hz, 2H). ^{13}C NMR ($CDCl_3$; δ, ppm): 178.84 (**Te=C**HN); 66.42 and 65.82 (**CH₂**O**CH₂**); 61.28 and 54.96 (**CH₂**N**CH₂**). ^{125}Te NMR ($CDCl_3$; δ, ppm): 888.2. Mass (EI mode; *m/e*): 229 (M^+, ^{130}Te), 98, 41. IR (KBr; cm^{-1}): 2977, 2918, 2858, 1655, 1503, 1440, 1294, 1230, 1108, 1026, 859, 698, 630. UV (cyclohexane; nm): 542, 365.

Synthesis of 1-Methyl-2-telluroxopyrroline (3d). Under an atmosphere of dry argon, a mixture of $(Me_3Sn)_2Te$ (770 mg, 1.70 mmol), toluene (15 mL), and Me_3Al (2 M in toluene, 1.9 mL, 3.8 mmol) were stirred in an aluminum-foil-wrapped 50 mL three-necked flask at 60−70 °C for 15 h to generate $(Me_2Al)_2Te$ (**2b**) in the form of a white suspension. To this suspension was added dioxane (5 mL) followed by 170 mg (1.71 mmol) of 1-methyl-2-pyrrolidinone (assay 99.5%). Following stirring at 80−90 °C for 3 h, the mixture (a deep purple solution) was evaporated and the residue then purified by flash column chromatography on Florisil (60−100 mesh) with CH_2Cl_2 as the solvent. Evaporation of the eluate gave 100 mg (yield 28%) of 1-methyl-2-telluroxopyrroline (**3d**) in the form of yellow crystals (mp 78.0−80.0 °C dec). Crystals for X-ray analysis were prepared by dissolving in CH_2Cl_2 followed by slow evaporation. Anal. Calcd for C_5H_9NTe: C, 28.50; H, 4.30; N, 6.65. Found C, 24.46; H, 4.27; N, 6.20. ^1H NMR ($CDCl_3$; δ, ppm): 3.60 (t, J = 7.61 Hz, 2H, CH_2**CH₂**N); 3.40 (s, 3H, **CH₃**N); 2.97 (t, J = 8.68 Hz, 2H, CH_2**CH₂**C=Te); 1.80−2.10 (m, 2H, CH_2**CH₂**CH_2). ^{13}C NMR ($CDCl_3$; δ, ppm): 190.30 (N**C**=Te); 59.96, 57.06, 43.56, 21.66. ^{125}Te NMR ($CDCl_3$; δ, ppm): 243.6. Mass (EI mode; *m/e*): 213 (M^+, ^{130}Te), 83, 55. IR (KBr; cm^{-1}): 2972, 2906, 1536, 1460, 1441, 1303, 1060, 999, 684, 605. UV−vis (cyclohexane; nm): 497, 356.

X-ray Diffraction. A yellow plate of **3a**, a red plate of **3b**, a yellow-orange plate of **3c**, and a yellow plate of **3d** were mounted on glass fibers at room temperature. Preliminary examination and data collection were performed on a Rigaku AFC5R (oriented graphite monochromator; Cu Kα radiation) at 163(2) K for **3a**, a Siemens R3M (oriented graphite monochromator; Mo Kα radiation) at 293 (2) K for **3b**, and a Siemens P4 single-crystal X-ray diffractometer (oriented graphite monochromatorr; Mo Kα radiation) at 193(2) K for **3c** and **3d**. Cell parameters for the four structures were calculated from the least-squares fitting for 25 high-angle reflections ($2\theta > 15°$). ω scans for several intense reflections indicated acceptable crystal quality. Scan width for data collection was $1.54 + 0.3 \tan \theta$ in ω with a fixed scan rate of 16°/min for **3a**. For **3b**, **3c**, and **3d**, the scan width was 2.0° in ω with a variable scan rate between 4 and 15°/min. For **3a**, weak reflections were rescanned (maximum of two rescans) and the counts for each scan were accumulated.

The three standards, collected every 150 reflections for **3a** and every 97 reflections for **3b**, **3c**, and **3d**, showed no significant trends. Background measurement by the stationary crystal and stationary counter technique was carried out at the beginning and the end of each scan for half the total scan time. An semi-empirical absorption correction was applied to **3a** (T_{max} = 0.989; T_{min} = 0.679) and **3b** (T_{max} = 0.999; T_{min} = 0.546), while an empirical absorption correction was applied for **3c** and **3d**.[16]

For **3a** three space groups (*C*2, *Cm*, or *C*2/*m*) are possible on the basis of the examination of the systematic absences. The inspection of intensities for reflections sensitive to a crystallographic mirror indicated that *C*2 was the best choice of the remaining space groups. Finally, attempts were made to solve and refine the structure in all three space groups; only the attempt in the space group *C*2 was successful. The *I*-centered cell may also be generated for **3a** by use of the matrix (0,0,−1; 010; 101).

All four structures were solved by direct methods[17] and refined by full-matrix least-squares methods.[18a] For **3c**, low-angle reflections were individually omitted due to interference from the beam stop. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 1.5 times the parameter of the attached atom. Neutral atom scattering factors and anomalous scattering factors were taken from ref 18b. Crystal structure parameters are given in Tables 1 and 2, and the atomic coordinates and isotropic thermal parameters for non-hydrogen atoms are given in the Supporting Information.

Results and Discussion

The syntheses of two telluroamides as isolable solids have been accomplished. Their crystal structures have been determined at low temperature. The syntheses and crystal structures of two selenoamides are also described. However, these tellurocarbonyl compounds display the typical characteristics of molecules which contain the C=Te bond, *viz.*, the rapid "shedding" of elemental tellurium due to the intrinsic thermodynamic instability of the tellurocarbonyl bond. This may be attributable to the poor overlap of the 2p(C)−5p(Te) π-bond. It is an intrinsic property of selenocarbonyls, *e.g.*, *N*,*N*-dimethylselenourea, and phosphine tellurides, R_3PTe, when initially prepared to show no signs of decomposition. As soon as decomposition does begin, however, as noted by the separation of metastable

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[15] The reaction carried out under the same conditions as in the case of **3a** gave a mixture of the desired selenoformamide (**3b**), the starting formamide, and methyl(4-nitrophenyl)amine.

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Table 1. Crystal Data and Structure Refinement Details for 3a and 3b

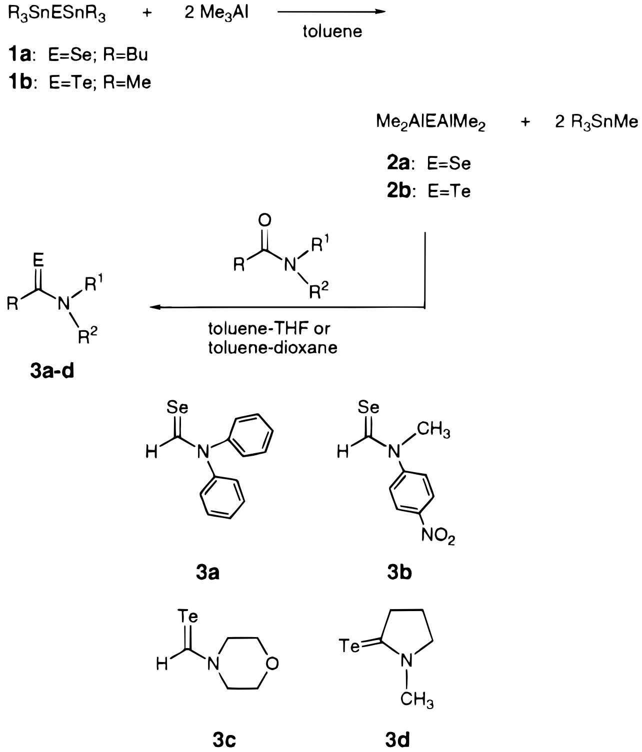
	3a	3b
empirical formula	$C_{13}H_{11}NSe$	$C_{16}H_{16}N_4O_4Se_2$
fw	260.19	486.25
temp/K	163(2)	293(2)
wavelength/Å	1.541 78	0.710 73
cryst syst	monoclinic	monoclinic
space group	*C*2	*P*2$_1$/*n*
unit cell dimens		
a/Å, α/deg	18.399(5), 90	16.344(3), 90
b/Å, β/deg	5.216(4), 121.43(2)	7.595(2), 118.09(3)
c/Å, γ/deg	13.753(4), 90	17.123(3), 90
V/Å^3, *Z*	1126.1(9), 4	1875.1(6), 4
density (calcd)/(Mg/m^3)	1.535	1.722
abs coeff/mm^{-1}	4.209	3.973
F(000)	520	960
crystal size/mm	0.28 × 0.22 × 0.08	0.3 × 0.3 × 0.1
θ range for data collection/deg	3.77–60.14	2.37–25.05
limiting indices	$0 \le h \le 20$, $0 \le k \le 5$, $-15 \le l \le 13$	$0 \le h \le 19$, $-9 \le k \le 0$, $-20 \le l \le 18$
no. of rflns collected	983	3437
no. of indep rflns	949 ($R_{int} = 0.0346$)	3315 ($R_{int} = 0.0243$)
abs cor	ψ-scan	ψ-scan
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
no. of data/restraints/params	949/1/137	3315/0/235
goodness of fit on F^2	1.070	1.016
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0384, wR2 = 0.1008	R1 = 0.0509, wR2 = 0.0943
R indices (all data)	R1 = 0.0401, wR2 = 0.1026	R1 = 0.1178, wR2 = 0.1215
extinction coeff	0.0030(5)	
largest diff peak and hole/(e/Å^3)	+0.490 and −0.900	+0.523 and −0.338

Table 2. Crystal Data and Structure Refinement Details for 3c and 3d

	3c	3d
empirical formula	C_5H_9NOTe	C_5H_9NTe
fw	226.37	210.73
temp/K	193(2)	193(2)
wavelength/Å	0.710 73	0.710 73
cryst syst	monoclinic	orthorhombic
space group	*P*2$_1$/*n*	Pbca
unit cell dimens		
a/Å, α/deg	5.0510(7), 90	8.219(3), 90
b/Å, β/deg	7.8839(8), 93.477(10)	12.483(3), 90
c/Å, γ/deg	18.261(2), 90	13.384(3), 90
V/Å^3, *Z*	725.92(2), 4	1373.2(6), 8
density (calcd)/(Mg/m^3)	2.075	2.039
abs coeff/mm^{-1}	4.009	4.219
F(000)	424	784
cryst size/mm	0.40 × 0.20 × 0.05	0.30 × 0.30 × 0.01
θ range for data collection/deg	2.23–30.09	3.04–24.99
limiting indices	$-1 \le h \le 6$, $-11 \le k \le 9$, $-11 \le l \le 11$	$-1 \le h \le 9$, $-1 \le k \le 14$, $-1 \le l \le 15$
no. of rflns collected	999	1148
no. of indep rflns	901 ($R_{int} = 0.0387$)	11 435 ($R_{int} = 0.0792$)
abs cor	Difabs	Difabs
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
no. of data/restraints/params	876/0/74	1143/6/64
goodness of fit on F^2	1.007	1.02
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0391, wR2 = 0.0828	R1 = 0.0653, wR2 = 0.0970
R indices (all data)	R1 = 0.0706, wR2 = 0.2005	R1 = 0.1718, wR2 = 0.1339
extinction coeff	0.0005(6)	
largest diff peak and hole/(e/Å^3)	+0.579 and −0.683	+1.142 and −1.031

monoclinic red selenium or black tellurium, the rates of decomposition increase. This we have observed in all such cases. Such behavior, apparently, is also the case for the telluroamides. It is our explanation, although not experimentally proven, that once decomposition begins, the separation of the free element serves to catalyze the decomposition. It is very likely that decomposition is initiated by exposure to light and also results from the intrinsic thermodynamic instabilities of the C=Se, C=Te, and P=Te bonds. The telluroamides reported here are too unstable for use as sources of telluride for the chemical deposition of thin films. The synthetic procedure, however, makes possible the synthesis of a variety of telluroamides, one or some of which may be sufficiently stable for such a purpose.

Scheme 1



Synthesis. Two crystalline selenoformamides (**3a**,**b**) and two telluroamides (**3c**,**d**) were prepared by the reaction between the corresponding amides and bis(dimethylaluminum) selenide (**2a**) or telluride (**2b**) generated *in situ via* the Sn–Al transmetalation reaction between bis(trialkyltin) selenide or telluride and 2 equiv of trimethylaluminum (Scheme 1).

N,*N*-Diphenylselenoformamide (**3a**) was isolated in the form of stable crystals in high yield (83%). It can be stored at room temperature without decomposition. The synthesis of *N*-methyl-*N*-(4-nitrophenyl)selenoformamide (**3b**) was carried out under conditions more mild than those for **3a**. The yield was much lower (25.4%), probably due to the presence of a strongly electron withdrawing group (O_2N–) which destabilizes the C=Se bond.

Telluroamides are much more unstable and very senstive to air, light, and moisture. They decompose during column purification. Consquently, during the syntheses of 4-(telluroformyl)morpholine (**3c**) and 1-methyl-2-telluroxopyrroline (**3d**), the reactions and purifications were carried out under a dry argon atmosphere and under conditions of minimum lighting. Also, bis(trimethyltin) telluride (**1b**) was used instead of its butyl analog $(Bu_3Sn)_2Te$ so that the byproduct Me_4Sn (bp 74–75 °C) could be easily removed by evaporation of the reaction mixture. The isolation of **3c** and **3d** through

Table 3. NMR Spectral Data of Seleno- and Telluroamides

	^{1}H NMR/δ^{a} (NC**H**=E)	^{13}C NMR/δ^{b} (N**C**=E)	^{77}Se NMR/δ^{c} (NC=**Se**)	^{125}Te NMR/δ^{d} (NC=**Te**)
3a	11.74 (8.67)^{e}	193.9 (161.7)^{e}	793.4	
3b	11.60 (8.71)^{e}	194.0 (161.5)^{e}	853.0	
3c	12.88 (7.99)^{e}	178.8 (160.8)^{e}		888.2
3d		190.3 (174.9)^{e}		243.6

[a] Measured in $CDCl_3$; in ppm referenced to the residual $CHCl_3$. [b] Measured in $CDCl_3$; in ppm referenced to $CDCl_3$. [c] Measured in $CDCl_3$ with PhSeSePh as the standard; in ppm relative to Me_2Se. [d] Measured in $CDCl_3$ with PhTeTePh as the standard; in ppm relative to Me_2Te. [e] For comparison, the chemical shifts of the corresponding amides are shown in parentheses.

column chromatography was accomplished as rapidly as possible. Compounds **3c** and **3d** were prepared in yields of 69.5% and 28%, respectively. These two tellurocarbonyl compounds possess sufficient chemical stability to allow for the determination of their crystal structures. However, they turn black on standing (deposition of tellurium) and decompose during storage, even in the freezing compartment of a refrigerator.

Spectroscopic Properties. IR spectral data (see Experimental Section) of selenoamides (**3a**,**b**) and telluroamides (**3c**,**d**) are not especially useful for determining the C=Se or C=Te frequencies, and the C=Se and C=Te absorption bands in the compounds reported in this study were not identified with any certainty. The NMR spectral data of compounds **3a**−**d** are listed in Table 3.

In the ^{1}H NMR spectra, the selenoformyl protons (**3a**, δ 11.74 ppm; **3b**, 11.60 ppm) were shifted downfield in comparison with the corresponding formyl protons (δ 8.67, 8.71 ppm). The telluroformyl proton of **3c** appeared at much lower field (δ 12.88 ppm). Also, the ^{13}C NMR chemical shifts of NC=E (E is Se or Te) are lower than those observed in the corresponding NC=O. These downfield shifts may result from the fact that the C=Se and C=Te groups, because the nuclei are so much larger, create a much higher anisotropy than the C=O group.

In the ^{77}Se NMR spectra, the chemical shifts of **3a** (δ 793.4 ppm) and **3b** (δ 853.0 ppm) are at higher fields than those of selenoketones (δ >1600 ppm),[19] but at lower fields than those of selenoureas (δ 18−200 ppm).[19,20] Similarly, the ^{125}Te chemical shifts of **3c** (δ 888.2 ppm) and **3d** (δ 243.6 ppm) are at much higher fields than that reported for a telluroketone (δ 2858 ppm),[3w] which bears a "pure" C=Te bond, and a telluroester (δ 1418 ppm)[8a] but at a lower field than has been reported for telluroureas (δ −167.82 to −200.03 ppm).[8d] The latter typically exist as the resonance form of N($^{+}$N=)C−Te^{-} rather than N(N)C=Te. The ^{77}Se or ^{125}Te NMR data for **3a**−**d** suggest that their true structures are probably better described by resonance forms **I** and **III**, in which **III** is the most important (Scheme 2). This is supported by the C—Te (2.043 Å in **3c** and 2.05 Å in **3d**), C—Se (1.816 Å in **3a** and 1.798, 1.789 in **3b**) and C—N (1.297−1.332 Å) bond distances measured for these molecules. These C—Te and C—Se distances are intermediate between values estimated for double (C=Te, 1.937 Å; C=Se, 1.737 Å) and single bonds (C—Te, 2.142 Å; C—Se, 1.942 Å).[21] The C—N distances are close to that of a typical C=N bond (1.28 Å).[22]

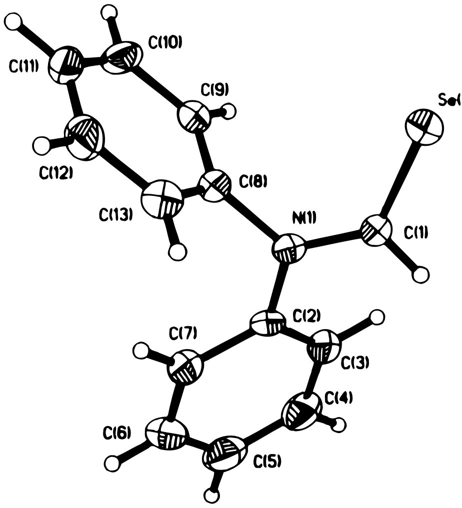
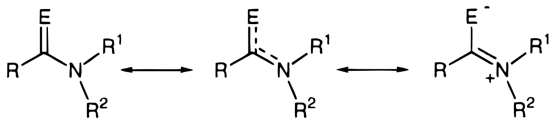


Figure 1. ORTEP diagram (50% thermal ellipsoids) of $C_{13}H_{11}NSe$ (**3a**).

Scheme 2

(E=Se, Te)



I **II** **III**

Crystal Structures. Transition-metal complexes of some telluroaldehydes, -ketones, and -ureas have been studied by X-ray crystallography.[3h,i,8e] In the case of free tellurocarbonyl compounds, only the crystal structure of 1,3-diisopropyl-4,5-dimethyl-2-telluroimidazoline, which actually bears a C—Te single bond (2.12 Å), has been reported.[8d] The successful synthesis of two crystalline telluroamides (**3c**,**d**) has enabled us to determine their crystal structures. Also, the structures of two selenoamides (**3a**,**b**) have been obtained. Their ORTEP drawings are shown in Figures 1−4, and the selected bond lengths and angles are listed in Tables 4−7.

The experimental C—Te multiple-bond distances reported in the literature are as follows: (A) 1.904 Å in S=C=Te, determined by microwave spectroscopy (MW);[23] (B) 1.923 Å in $Cl_2Os(CO)(CTe)(PPh_3)_2$;[24] (C) 2.043−2.15 Å in three- or four-coordinated tellurium compounds;[25] (D) 1.987−2.21 Å in the transition-metal complexes of tellurocarbonyls.[3h,i,8e] The shorter C—Te bond distances in the first two examples are due to carbon sp hybridization, which forms a C(sp)—Te rather than a C(sp^{2})—Te multiple bond. In cases C and D the C—Te bond distances fall within the range 2.007−2.309 Å (number of C—Te single bonds reported 483, mean 2.128 Å),[26]

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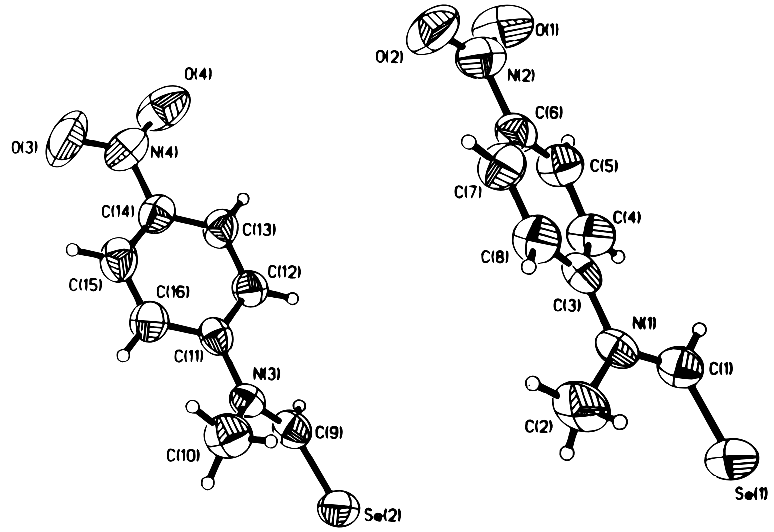

Figure 2. ORTEP diagram (50% thermal ellipsoids) of $C_8H_8N_2O_2Se$ (**3b**).

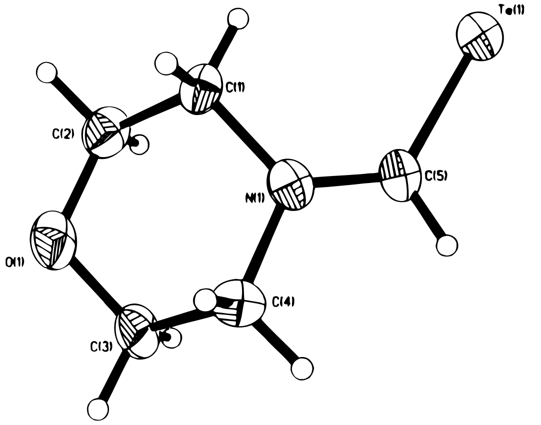

Figure 3. ORTEP diagram (50% thermal ellipsoids) of C_5H_9NOTe (**3c**).

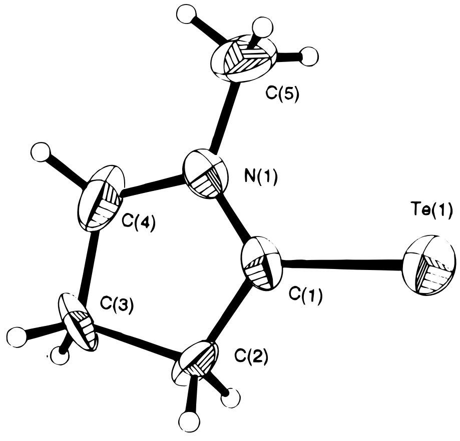

Figure 4. ORTEP diagram (50% thermal ellipsoids) of C_5H_9NOTe (**3d**).

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 3a

Se(1)−C(1)	1.816(6)	N(1)−C(2)	1.428(8)
N(1)−C(1)	1.332(8)	N(1)−C(8)	1.454(7)
N(1)−C(1)−Se(1)	128.2(4)	C(1)−N(1)−C(8)	119.6(5)
C(1)−N(1)−C(2)	121.8(5)	C(2)−N(1)−C(8)	118.6(4)

except for a tungsten telluroketone complex, in which the C−Te bond length is 1.987 Å.[3i] The experimentally measured C−Te bond distances in this study are 2.043(9) Å in **3c** and 2.05(2) Å in **3d**, which well fall within the range of values for double bonds as seen in the CSD database (number reported 6, mean 2.06(3) Å, range 1.923−2.122 Å).[26]

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 3b

Se(1)−C(1)	1.798(6)	Se(2)−C(9)	1.789(6)
N(1)−C(1)	1.312(7)	N(3)−C(9)	1.319(7)
N(1)−C(2)	1.459(7)	N(3)−C(10)	1.463(7)
N(1)−C(3)	1.434(7)	N(3)−C(11)	1.419(7)
N(1)−C(1)−Se(1)	127.1(5)	N(3)−C(9)−Se(2)	128.2(5)
C(1)−N(1)−C(2)	119.9(5)	C(9)−N(3)−C(10)	120.3(5)
C(1)−N(1)−C(3)	121.3(5)	C(9)−N(3)−C(11)	122.1(5)
C(2)−N(1)−C(3)	118.7(5)	C(10)−N(3)−C(11)	117.5(5)

Table 6. Selected Bond Lengths (Å) and Angles (deg) for 3c

Te(1)−C(5)	2.043(9)	N(1)−C(1)	1.459(13)
N(1)−C(57)	1.297(11)	N(1)−C(4)	1.477(11)
N(1)−C(5)−Te(1)	128.6(8)	C(5)−N(1)−C(1)	126.0(8)
C(5)−N(1)−C(4)	121.6(10)	C(1)−N(1)−C(4)	112.4(8)

Table 7. Selected Bond Lengths (Å) and Angles (deg) for 3d

Te(1)−C(1)	2.05(2)	N(1)−C(4)	1.47(2)
N(1)−C(1)	1.32(2)	N(1)−C(5)	1.45(2)
N(1)−C(1)−Te(1)	126.0(13)	C(1)−N(1)−C(5)	127(2)
C(1)−N(1)−C(4)	115(2)	C(4)−N(1)−C(5)	118(2)
C(2)−C(1)−Te(1)	125.5(12)	N(1)−C(1)−C(2)	108.5(14)

Also, the C−Se bond distances in **3a** (1.816(6) Å) and **3b** (1.789(6) and 1.798(6) Å) fall within the range of 1.608 to 2.021 Å (number reported 162, mean 1.857(4) Å) for C=Se bonds found in the CSD database.[26] They are shorter than the values reported for selenoureas (1.82−1.87 Å)[27] and the metal complexes of selenocarbonyl compounds[28] but longer than those in selenoacetaldehyde ($CH_3C(H)=Se$; 1.758 Å, determined by microwave spectroscopy (MW))[29] and selenocarbonyl

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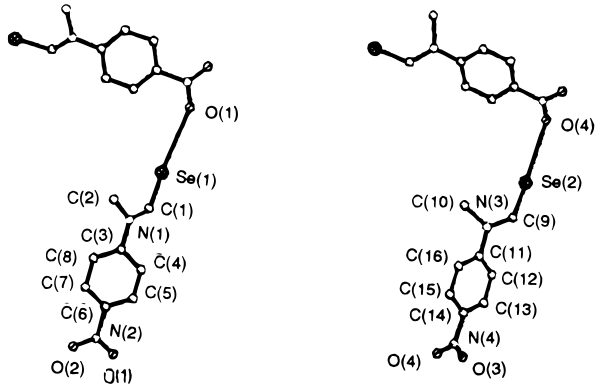

Figure 5. Intermolecular distances Se···O in **3b**. Se(1)···O(1) is 3.279(5) Å; Se(2)···O(4) is 3.116(5) Å.

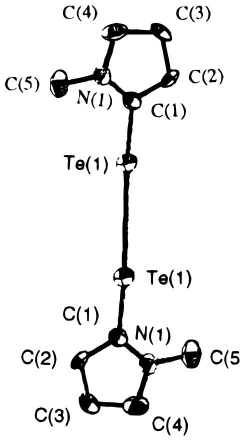

Figure 6. Intermolecular distance Te···Te in **3d**. Te(1)···Te(1) is 3.801(2) Å.

difluoride ($F_2C{=}Se$; 1.743 Å, measured by electron diffraction (ED)).[30] It is noteworthy that the C—Se bond distances in **3b** are very close to the value of 1.790 Å reported for the "pure" C=Se bond in a selenoketone, 4,4′-dimethoxyselenobenzophenone.[31]

The C—Te double- and single-bond distances estimated from the Pauling values[21] are 1.937 and 2.142 Å, respectively. The C—Se double- and single-bond distances are estimated at 1.737 and 1.942 Å. The experimentally measured C—Te and C—Se bond distances in the present work lie between the values calculated for the single and double bonds. In the four compounds, for the nitrogen atom bonded to tellurocarbonyl or selenocarbonyl carbons, the C—N distances are 1.297 (**3c**), 1.32 (**3d**), 1.332 (**3a**), and 1.312 Å (**3b**); very close to the value of 1.287 Å estimated for the C=N double bond. Also, the bond angles around the nitrogen atom bonded to the telluro- or selenocarbonyl carbon are close to 120°. All of these bond distances (C—Te, C—Se, and C—N) and bond angles reveal that in the solid state of telluroamides (**3c**,**d**) and selenoamides (**3a**,**b**), form **III** contributes more to the structures (Scheme 2).

In addition, Se···O intermolecular contacts are present in **3b**, while a short Te···Te distance is observed in **3d**. In **3b** the intermolecular distances Se(1)···O(1) and Se(2)···O(4) are 3.279(5) and 3.116(5) Å, respectively, while the Te(1)···Te(1) distance in **3d** is 3.801(2) Å. The Te···Te distance is considerably shorter than the expected nonbonded (van der Waals) distance of 4.40 Å.[32] The Se···O distances are only slightly shorter than the sum of their van der Waals radii (3.40 Å). This is shown in stereographic projections (Figures 5 and 6). The importance of chalcogen—oxygen interactions in controlling the geometries of small and large molecules has been noted previously.[33] This study further illustrates unusual attractive interactions which exist between chalcogen atoms and oxygen atoms.

Acknowledgment. This research was supported by grants from the Robert A. Welch Foundation, Houston, TX, and the National Science Foundation (Grant No. INT-9402007). We wish to thank Dr. E. A. Meyers for his helpful comments on the crystal structures.

Supporting Information Available: Listings of all bond distances and angles, anisotropic displacement parameters, hydrogen atom coordinates and isotropic displacement parameters, and analytical and spectral data for compounds **3a**—**d** (45 pages). Ordering information is given on any current masthead page.

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