Synthesis, Structure, and Reactivity of Organochalcogen (Se, Te) Compounds Derived from 1-(*N*,*N*-Dimethylamino)naphthalene and *N*,*N*-Dimethylbenzylamine

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A series of intramolecularly coordinated organochalcogen compounds incorporating the 8-(dimethylamino)-1-naphthyl and 2-[(dimethylamino)methyl]phenyl groups has been synthesized. All the compounds were synthesized using the ortholithiation methodology. Insertion of elemental selenium into the Li−C bond of RLi (**6**) (R = 8-(dimethylamino)-1-naphthyl) afforded the lithium areneselenolate RSeLi (**7**). Oxidative workup of **7** yielded the yellow diselenide **8** in good yield. Reaction of **8** with a stoichiometric amount of sulfuryl chloride gave the monochloro derivative (**9**). Controlled bromination of diselenide (**8**) with bromine in carbon tetrachloride gave the stable selenenyl bromide (**10**). Compound **8** underwent facile reaction with a stoichiometric amount of iodine to give the corresponding novel monoiodo compound (**11**) in which selenium is covalently bonded to iodine. Attempts to synthesize the chalcogenides, R_2E, **12** (E = Se) and **13** (E = Te), by the reaction of **6** with $Se(dtc)_2$ and $Te(dtc)_2$ (dtc = diethyldithiacarbamate), respectively, were unsuccessful. The reaction of **6** with $Te(dtc)_2$ afforded the stable RTe(dtc) (**14**) instead of the expected telluride R_2Te (**13**). In contrast, the reaction of R′Li (**17**) (R′ = 2-[(dimethylamino)methyl)phenyl] with $Se(dtc)_2$ and $Te(dtc)_2$ afforded the expected selenide R'_2Se (**18**) and telluride R'_2Te (**19**), respectively, in moderate yields. The compounds were characterized by elemental analysis, NMR (^1H, ^{13}C, ^{77}Se, ^{125}Te), and mass spectral techniques. The structures of the compounds **9**, **11**, **14**, and **18** were determined by X-ray crystallography. Although N···E (E = Se or Te) nonbonded interactions are present in the solid state in all the derivatives, in solution the pyramidal inversion at the nitrogen center is not blocked, and as a result, the NMe_2 signals are observed as sharp signals in the ^1H NMR spectra.

Introduction

Organochalcogens having an intramolecular E···N interaction (E = Se, Te) have attracted considerable current interest. In particular, the organoselenium derivatives find applications as (a) electrophilic and nucleophilic reagents in asymmetric synthesis where the intramolecular Se···N interactions induce conformational rigidity in the molecule and these interactions are assumed to play a determinant role in chirality transfer,[1] (b) ligands in achiral and chiral catalysis,[2] (c) ligands for the isolation of monomeric and stable precursors for MOCVD of semiconductors,[3] (d) hypercoordinated derivatives,[4] and (e) synthetic models for glutathione peroxidase where the Se···N interactions play a key role in stabilizing the key intermediate selenenic acid.[5]

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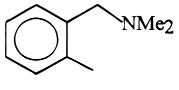
We have previously reported a range of intramolecularly coordinated organotellurium compounds[6] featuring **1**, **2**, **3**, and **4**. In each case, it was observed that the amine/imine nitrogen was coordinated to the tellurium atom. In the case of organotellurium derivatives of **1** and **4**, the amino group present in the derivatives of **4** was more strongly coordinated to the chalcogen. This difference may arise from the fact that the ligand **1** is very flexible whereas ligand **4** is rigid and planar.



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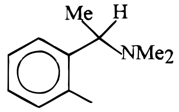

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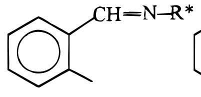

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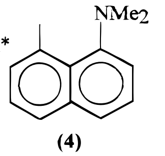

(4)

Although organoselenenyl halides have become widely used reagents for synthetic organic chemistry, their systematic study including structures has found limited investigations. We have recently reported the synthesis of a series of intramolecularly coordinated organoselenium compounds derived from *N*,*N*-dimethylbenzylamine along with the structures of bis[2-dimethylaminomethyl)phenyl] diselenide and [2-(dimethylaminomethyl)phenyl] selenium bromide.[2c] The synthesis, structure, and thiol peroxidase activity of a series of intramolecularly coordinated novel diselenides also were reported.[7] It was thought worthwhile to extend the range of stable selenenyl halides using the more rigid and planar substrate, 1-(dimethylamino)naphthalene. In this paper we report examples of structurally characterized selenenyl chloride and iodide. Here we also compare the structure and reactivity of organochalcogen (Se, Te) compounds derived from 1-(dimethylamino)naphthalene with those derived from *N*,*N*-dimethylbenzylamine. It is worth noting that a few organoselenium derivatives of **4** have been reported by Furukawa et al., and the selenation was achieved by the reaction of MeSeCN with 8-(dimethylamino)-1-naphthyllithium.[4d] A number of related 1,8-diaryl and dialkyl substituted chalcogenonaphthalenes have been reported in the literature, and Se···X (X = S, Se, F, Cl) interactions have been analyzed by Furukawa et al.[8] and Nakanishi et al.[9] Very recently, Nakanishi et al. have reported the observation of novel F···Se−C intramolecular interaction in 8-fluoro-1-(*p*-anisylselanyl)naphthalene.[10]

Experimental Section

General Procedures. All the reactions were carried out under N_2 atmosphere. Solvents were purified and dried by standard techniques.[11] All chemicals used, e.g., *N*,*N*-dimethylnaphthylamine (Fluka) and *n*-butyllithium (E. Merck), were reagent grade and were used as received. $Te(dtc)_2$ and $Se(dtc)_2$ were prepared as reported.[12] Melting points were recorded in capillary tubes and are uncorrected. ^{1}H, ^{13}C, ^{77}Se, and ^{125}Te NMR spectra were obtained at 300, 75.42, 57.22, and 94.75 MHz, respectively in $CDCl_3$ on a Varian VXR 300S spectrometer. Chemical shifts are cited with respect to $SiMe_4$ as internal (^{1}H and ^{13}C) and Me_2Se, Me_2Te (^{77}Se and ^{125}Te) as external standard. Elemental analyses were performed on a Carlo-Erba model 1106 elemental analyzer. Fast atom bombardment (FAB) mass spectra were recorded at room temperature on a JEOL SX 102 DA-6000 mass spectrometer/data system using xenon (6 kV, 10 mV) as the ionizing gas. The acceleration voltage was 10 kV, and *m*-nitrobenzyl alcohol was used as the matrix with positive-ion detection. In the case of isotopic patterns the value given is for the most intense peak.

Synthesis of 8-(Dimethylamino)-1-naphthylselenium(II) Chloride (9). To a solution of bis[8-(dimethylamino)-1-naphthyl] diselenide[7] (**8**) (0.5 g, 1 mmol) in CCl_4 (25 mL) at room temperature was added a solution of SO_2Cl_2 (0.13 g, 1 mmol) in CCl_4. The reaction mixture was stirred for 1 h at room temperature. The resulting solution was concentrated to give a white product. This was recrystallized from CH_2Cl_2/ether mixture to give white crystals of **9** in 55% yield (0.16 g); mp 166−168 °C (decomp). Anal. Calcd for $C_{12}H_{12}NSeCl$: C, 50.64; H, 4.25; N, 4.92. Found: C, 50.49; H, 4.14; N, 4.74. ^{1}H NMR ($CDCl_3$): δ 3.13 (s, 6H), 7.42 (d, 1H), 7.65−7.51 (m, 2H), 7.73 (dd, 1H), 7.85 (dd, 1H) 8.18 (dd, 1H). ^{77}Se NMR($CDCl_3$): δ 1060.59.

Synthesis of 8-(Dimethylamino)-1-naphthylselenium(II) Bromide (10). To a solution of bis[8-(dimethylamino)-1-naphthyl] diselenide (**8**) (0.5 g, 1 mmol) in CCl_4 (25 mL) was added a solution of Br_2 (0.16 g, 1 mmol) in CCl_4. The addition was carried out dropwise over a period of 0.5 h at 0 °C and then allowed to come to room temperature. The reaction mixture was stirred for an additional 3 h at room temperature. Evaporation of the solvent gave a brown solid, which was recrystallized from CH_2Cl_2/ether. Yield: 80% (0.26 g), mp 148−150 °C. Anal. Calcd for $C_{12}H_{12}NSeBr$: C, 43.16; H, 3.60; N, 4.07. Found: C, 43.24; H, 3.68; N, 4.26; ^{1}H NMR ($CDCl_3$): δ 3.12 (s, 6H), 7.42 (d, 1H), 7.6−7.52 (m, 2H), 7.76 (d, 1H), 7.86 (d, 1H), 8.2 (d, 1H). ^{13}C NMR($CDCl_3$): δ 51.27, 117.12, 125.01, 126.14, 127.38, 127.79, 129.02, 130.2, 134.63, 147.17. ^{77}Se NMR ($CDCl_3$): δ 1015.88.

Synthesis of 8-(Dimethylamino)-1-naphthylselenium(II) Iodide (11). To a cold solution of bis[8-(dimethylamino)-1-naphthyl] diselenide (0.5 g, 1 mmol) in CCl_4 (25 mL) was added a solution of iodine (0.25 g, 1 mmol) in CCl_4. The reaction mixture was stirred at 0 °C for 1 h and at room temperature for an additional 2 h. The solution was evaporated to give a red solid, which was recrystallized from CH_2Cl_2/ether to give brick red crystals. Yield: 75% (0.56 g), mp 132−134 °C. Anal. Calcd for $C_{12}H_{12}NSeI$: C, 38.32; H, 3.22; N, 3.72. Found: C, 38.47; H, 3.48; N, 3.68. ^{1}H NMR ($CDCl_3$): δ 3.01 (s, 6H), 7.45 (dd, 1H), 7.56−7.48 (m, 2H), 7.77 (d, 1H), 7.83 (dd, 1H), 8.12 (dd, 1H). ^{13}C NMR ($CDCl_3$): δ 50.34, 117.03, 125.71, 126.11, 127.54, 128.81, 129.47, 132.04, 134.58, 147.22. ^{77}Se NMR ($CDCl_3$): δ 951.

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Table 1. Crystal Data and Structure Refinement for 9, 11, 14, and 18

	compound			
	9	**11**	**14**	**18**
empirical formula	$C_{12}H_{12}ClNSe$	$C_{12}H_{12}INSe$	$C_{17}H_{22}N_2S_2Te$	$C_{18}H_{24}N_2Se$
fw	284.64	376.09	446.09	347.35
cryst syst	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	Pbca	Pbca	$P2_1/c$	$P2_1/n$
a (Å)	6.9907(10)	7.5300(10)	10.496(2)	10.1630(12)
b (Å)	11.725(3)	12.023(2)	11.7899(11)	5.5209(8)
c (Å)	29.301(3)	28.704(4)	16.094(3)	32.125(5)
α (deg)	90	90	90	90
β (deg)	90	90	108.427(12)	97.242(10)
γ (deg)	90	90	90	90
V (Å^3)	2401.7(7)	2598.7(6)	1889.5(5)	1788.1(4)
Z	8	8	4	4
D(calcd) (Mg/m^3)	1.574	1.923	1.568	1.290
temp (K)	293(2)	293(2)	293(2)	293(2)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
abs coeff (mm^{-1})	3.313	5.235	1.794	2.096
no. of obsd reflens [$I > 2\sigma$]	2418	2666	4060	4037
final $R(F)$ [$I > 2\sigma$]^a	0.0513	0.0438	0.0318	0.0399
$wR(F^2)$ indices [$I > 2\sigma$]	0.1121	0.0971	0.0804	0.0847
no. of data/restraints/parameters	2418/0/150	2665/0/150	4060/0/225	4037/0/219
goodness of fit on F^2	1.050	1.025	1.037	1.049

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

Synthesis of 8-[(Dimethylamino)-1-naphthyl]tellurium-diethyl Dithiacarbamate (14). To a suspension of 8-(dimethylamino)-1-naphthyllithium (**6**) (1.06 g, 6 mmol) in ether (20 mL) was added Te(dtc)$_2$ (1.27 g, 3 mmol) at room temperature under the brisk flow of nitrogen. The reaction mixture was stirred for 0.5 h and then poured into a beaker containing cold water (500 mL). The compound was extracted with ether (3 × 50 mL), dried over sodium sulfate, and concentrated in vacuo to give a yellow oil. The crystals of compound **14** were obtained from an acetone/pentane mixture upon cooling. Yield: 70% (1.83 g), mp 142−144 °C. Anal. Calcd for $C_{17}H_{22}N_2S_2Te$: C, 54.55; H, 6.36; N, 6.36. Found: C, 54.69; H, 6.23; N, 6.61. NMR (CDCl$_3$): δ 1.27−1.42 (m, 6H), 3.08 (s, 6H), 4.01−4.15 (m, 4H), 7.41 (dd, 1H), 7.5−7.45 (m, 2H), 7.69 (dd, 1H), 7.75 (dd, 1H), 7.85 (dd, 1H). ^{13}C NMR (CDCl$_3$): δ 11.8, 13, 48.4, 50, 118.2, 120.2, 125.7, 126.1, 127.6, 128.3, 131.9, 132.5, 135.5, 149.3. ^{125}Te (CDCl$_3$): δ 1124.0.

Synthesis of α,α′-Bis[8-(dimethylamino)-1-naphthylselenenyl]-*o*-xylene (15). To a solution of **7** (1.54 g, 6 mmol) in ether (20 mL) was added dropwise, a solution of α,α′-dibromo-*o*-xylene (0.78 g, 3 mmol) in ether (15 mL) and stirring was continued for 12 h at room temperature. The resulting mixture was washed with water, dried over sodium sulfate, and evaporated to give a yellow oil, which solidified upon keeping overnight at room temperature. The compound was recrystallized by slow evaporation of a CH$_2$Cl$_2$/hexane solution. Yield: 35% (1.23 g); mp 146−148 °C. Anal. Calcd for $C_{32}H_{32}N_2Se_2$: C, 63.79; H, 5.32; N, 4.65. Found: C, 63.85; H, 5.41; N, 4.84. ^{1}H NMR (CDCl$_3$): δ 3.01 (s, 6H), 4.49 (d, 1H), 5.80 (d, 1H), 7.15−7.96 (m, 13H). ^{13}C NMR (CDCl$_3$): δ: 46.51, 48.83, 119.41, 121.05, 126.13, 126.50, 127.08, 127.36, 128.04, 129.7, 132.4, 135.9, 135.93, 148.4. ^{77}Se NMR (CDCl$_3$): δ 545.9.

Synthesis of Bis[(*N*,*N*-dimethylamino)benzyl] Selenide (18). A stirred solution of *N*,*N*-dimethylbenzylamine (**16**) (1.53 mL, 10.2 mmol) in dry ether (50 mL) was treated dropwise with a 1.6 M solution of n-BuLi in hexane (7.5 mL, 12 mmol) under nitrogen. After stirring for 24 h at room temperature a white slurry of the lithiated product was obtained.[6c] To this Se(dtc)$_2$ (2 g, 5.1 mmol) was added under the brisk flow of nitrogen. The reaction mixture was stirred for 0.5 h and then poured into a beaker containing cold water (500 mL). The compound was extracted with ether (3 × 50 mL), dried over sodium sulfate, and concentrated in vacuo to give a white crystalline product. Recrystallization of this from methanol afforded white needles of **18**. Yield: 97% (1.72 g); mp 62−64 °C Anal. Calcd for $C_{18}H_{24}N_2Se$: C, 62.24; H, 6.96; N, 8.06. Found: C, 61.8; H, 7.02; N, 7.88. ^{1}H NMR (CDCl$_3$): δ 2.23 (s, 12H), 3.52 (s, 4H), 7.04−7.38 (m, 8H). ^{13}C NMR (CDCl$_3$): δ 45.17, 64.18, 127.02, 127.81, 129.78, 134.31, 134.52, 140.79.^{77}Se NMR (CDCl$_3$): δ 340.8. MS: m/z 347 (M$^+$, 100, $C_{18}H_{24}N_2Se$), 303 ($C_{16}H_{18}NSe$), 259 ($C_{14}H_{12}Se$), 214 ($C_9H_{12}NSe$), 134 ($C_9H_{12}N$), 170 (C_7H_6Se).

Synthesis of Bis[(*N*,*N*-dimethylamino)benzyl] Telluride (19)[6c]. To a solution of **17** (1.40 g,10 mmol) in ether (25 mL) was added Te(dtc)$_2$ (1.97 g, 5.1 mmol) under a brisk flow of nitrogen. The reaction mixture was stirred for 0.5 h and poured into a beaker containing cold water (500 mL). The compound was extracted with ether (3 × 50 mL), dried over sodium sulfate, and concentrated in vacuo to give a white crystalline product in 78% yield. Recrystallization from methanol afforded white needles of **19**, mp 100−102 °C (lit. 98 °C). Anal. Calcd for $C_{18}H_{24}N_2Te$: C, 54.6; H, 6.11; N, 7.07. Found: C, 54.76; H, 6.24; N, 6.89. ^{1}H and ^{13}C NMR data were in full accordance with the reported values.[6c]

X-ray Crystallographic Study. The diffraction measurements for compounds **9**, **11**, **14**, and **18** were performed at room temperature (293 K) on a Siemens R3m/V diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.7170$ Å). The unit cell was determined from 25 randomly selected reflections using the automatic search index and least-squares routine. The data were corrected for Lorentz, polarization, and absorption effects. The data were monitored by measuring two standard reflections every 60 min of X-ray exposure time. The structures were solved by routine heavy-atom using SHELXS 86[13] and Fourier methods and refined by full-matrix least-squares with the non-hydrogen atoms anisotropic and hydrogens with fixed isotropic thermal parameters of 0.07 Å^2 using the SHELXL 93 program.[14] The hydrogens were partially located from difference electron-density maps, and the rest were fixed at calculated positions. Scattering factors were from common sources.[15] Some details of data collection and refinement are given in Table 1.

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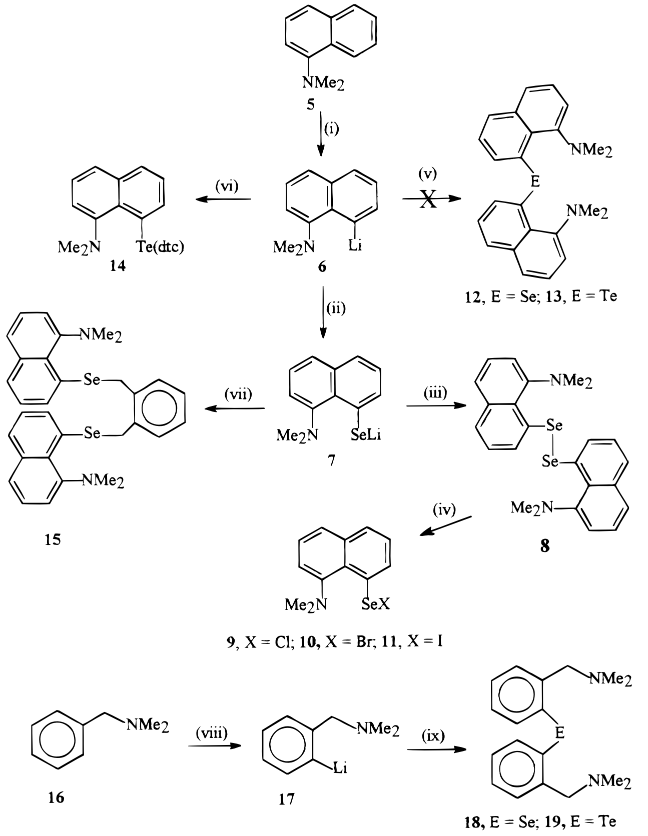
Scheme 1[a]



[a] Reagents and Condition: (i) n-BuLi, ether, r.t.; (ii) Se powder, r.t.; (iii) O_2 (iv) SO_2Cl_2, Br_2 or I_2, CCl_4, 0 °C; (v) 0.5 $E(dtc)_2$ (E = Se, Te); (iv) 0.5 $Te(dtc)_2$; (vii) α,α′-dibromo-*o*-xylene, r.t.; (viii) n-BuLi, ether, r.t.; (ix) $E(dtc)_2$ (E = Se, Te).

Results and Discussion

Bis[8-(dimethylamino)1-naphthyl] diselenide[7] (**8**) was synthesized from [8-(dimethylamino)-1-naphthyl]lithium etherate (**6**) and elemental selenium (Scheme 1) followed by mild oxidation. The light yellow solution of the lithium naphthaleneselenolate (**7**) was obtained by the reaction of **6** with finely powdered selenium, which dissolved completely within 3 h. Aqueous oxidative workup of the lithium selenolate then afforded the yellow diselenide (**8**). Reaction of **8** with a stoichiometric amount of sulfuryl chloride gave the monochloro compound (**9**) in good yield. The compound **9** was found to be quite stable to moisture and air due to the presence of a basic amino group which coordinates to the selenium and stabilizes the Se−Cl bond (vide infra). Controlled bromination of **8** (1:1) afforded the selenium(II) bromide (**10**), and with an excess of bromine (1:3), selenium(IV) tribromide was obtained. The $RSeBr_3$ compound was unstable when isolated and decomposed over a period of 2 h to give **10**. This is inconsistent with the recent report that the oxidative addition of Br_2 to Se(II) compound is a reversible process.[16]

It is known that diorgano selenides and diorgano diselenides undergo reaction with iodine to give only charge-transfer adducts.[17] Stable binary compounds between elemental iodine and selenium, having very similar electronegativities,[18] have not been studied extensively. Du Mont et al. reported the isolation and structural characterization of a stable iodoselenide using bulky aryl substituents.[19] They also observed that a slight reduction in the steric bulkiness again led to the isolation of the charge-transfer adduct, but a stable Se−I covalent bond could not be obtained.[20] When compound **8** was treated with a stoichiometric amount of iodine, a novel monoiodide (**11**) having a covalent Se−I bond was obtained in nearly quantitative yield (vide infra).

The metathesis reactions of RLi with $Se(dtc)_2$ (dtc = diethyldithiacarbamate) and $Te(dtc)_2$ were expected to give the novel tridentate ligands of the type R_2Te. All attempts to synthesize R_2Se (**12**) and R_2Te (**13**) by the reactions of **6** with $Se(dtc)_2$ or $Te(dtc)_2$ were unsuccessful. However, the reaction of **6** with $Te(dtc)_2$ afforded RTe(dtc) (**14**) instead of the expected R_2Te (**13**). The formation of RTe(dtc) was observed irrespective of the molar ratio of **6** and $Te(dtc)_2$. This is consistent with our earlier observations in the attempted synthesis of R_2Te (**13**). In this particular case when the lithiated compound **6** underwent reaction with TeI_2 to obtain R_2Te, it only gave RTeI as a stable compound in low yield.[6g] To confirm whether the formation of RTeX (X = I, dtc) depends on the nature of aryl group or on the nature of the electrophile, we investigated the reaction of R′Li (**17**) derived from the more flexible *N*,*N*-dimethylbenzylamine with $Se(dtc)_2$. In this case we isolated the expected R'_2Se (**18**) in high yield, and there was no indication of the formation of R′Se(dtc). It is worth noting that when *N*,*N*-dimethylbenzylamine underwent reaction with $Te(dtc)_2$ or TeI_2, it was possible to isolate pure R'_2Te (**19**), while the formation of R′Te(dtc) or R′TeI was not observed. The yield of **19** was slightly higher when $Te(dtc)_2$ was used as the tellurium source in place of TeI_2. From these results it is clear that the nature of organic group affects the formation of the product. Since the ligand derived from 1-dimethylaminonaphthalene is sterically bulkier than the simple 2-(dimethylamino)phenyl ligand, the R_2Se or R_2Te compounds could not be isolated. Reaction of **7** with α,α′-dibromo-*o*-xylene afforded the novel tetradentate ligand stable benzylic compound (**15**).

The compounds in solution were characterized by spectroscopic means. In solution, the Se···N and Te···N interaction are considered to be weak as the two methyl groups on nitrogen in **8**, **9**, **10**, **11**, **14**, and **15** are observed as a sharp singlet in ^1H and ^{13}C NMR spectra. This probably indicates a pyramidal inversion at the nitrogen center of the NMe_2 group in solution. However, in the ^1H NMR spectra, significant downfield shifts for the methyl protons were observed for **9**, **10**, and **11**, where there are more electronegative atoms such as Cl, Br, and I attached to Se compared to the free amine. The maximum downfield shift was observed in the case of **9**, where selenium is bonded to the highly electronegative chlorine atom. All the compounds except $RSeBr_3$ are quite stable in solution, and there was no indication of the formation of any dissociated products.

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The Se(IV) tribromide, however, dissociated to RSeBr. It is worth noting that in the case of **11** there was no indication of the formation of diselenide in solution. This is in contrast with previous results on RSeI compounds, where the compounds were unstable and decomposed in solution to give peaks for the corresponding diselenides.[16] The ^{1}H NMR spectrum of compound **15** is very interesting. Although the signal due to NMe_2 protons is a sharp singlet, the signal due to benzylic protons was resolved into an AB quartet at room temperature. The results imply that the benzylic protons become diastereotopic due to the intramolecular Se···N interaction in solution.

The ^{77}Se chemical shifts are cited in the Experimental Section and found to be sensitive to the nature of the substituent group bonded to the selenium atom. In the case of the selenenyl halides, a large deshielding is observed with respect to the diselenide. McFarlane and Wood have reported that the selenium resonances are increasingly deshielded as the electronegativity of the substituent attached increases.[21] The ^{77}Se chemical shifts for compounds RSeCl (**9**) (1060.6 ppm) and RSeBr (**10**) (1015.9 ppm) are very close to the values for RSeCl (1050.3 ppm) and RSeBr (1010 ppm) [R = (*N*-cyclohexyl-*N*-methylamino)benzyl] reported by Tomoda et al.[4e] A sharp signal at 545.9 ppm observed for **15** indicates that the two selenium nuclei present in the molecule are equivalent. The ^{77}Se chemical shift for R'_2Se (**18**) is relatively upfield shifted (340.8 ppm) compared with the diselenide (430.0 ppm).[2c] In this case, the two nitrogen atoms may interact with the central atom simultaneously in solution to increase the electron density around the selenium. The above results clearly suggest that the intramolecular Se···N coordination results in a downfield shift of ^{77}Se NMR.

It is interesting to compare the ^{77}Se chemical shift values of the compounds derived from **5** with the corresponding selenium compounds derived from **16**. Generally, the ^{77}Se NMR chemical shifts of selenium compounds derived from *N*,*N*-dimethylbenzylamine (**16**) appear at a upfield position compared with the analogous compounds derived from *N*,*N*-dimethylnaphthylamine (**5**). For example, the chemical shifts of RSeBr (**10**) (1015.9 ppm) and RSeI (**11**) (951.1 ppm) are much higher than that of R′SeBr (987 ppm) and R′SeI (818 ppm) derived from *N*,*N*-dimethylbenzylamine. The above observations are quite similar to those observed for the related phosphorus derivatives of the 2-[(dimethylamino)methyl]phenyl ligand and 8-(dimethylamino)-1-naphthyl ligand.[22] The rigidity of the naphthalene skeleton imposes a close approach of the potential donor nitrogen and acceptor selenium. This is clearly indicated from the shorter Se···N distance in **8** compared with the Se···N distance in $(2\text{-}NMe_2CH_2C_6H_4)_2Se_2$ (vide infra). Although ^{1}H NMR data are not very informative about the Se···N interaction in solution, the ^{77}Se NMR data and the observed Se···N distances in the solid state indicate a much stronger Se···N interaction in these compounds compared with analogous compounds derived from *N*,*N*-dimethylbenzylamine.

Molecular Structure of 8. The details of the structure of compound **8** will be reported elsewhere.[7] Here we present only the salient feature of the structure. The Se(1A)−Se(1B) bond length of the diselenide [2.383(2) Å] is slightly higher than the sum of the Pauling single bond covalent radii (2.34 Å).[23] This value is also higher than the corresponding bond lengths reported for related diselenides bis[2-(dimethylaminomethyl)phenyl] diselenide (2.357(1) Å), $Se_2\{(C_6H_5)Fe[C_5H_3(CH_2NMe_2)]\}_2$ (2.36 Å),[24] and 2,2′-diselenobis(*N*-cyclohexyl-*N*-methylbenzylamine) (2.362(1) Å).[25] The larger Se−Se distance is presumably due to a strong Se···N interaction, which leads to lengthening of the trans Se−Se bond. The distances Se(1A)···N(1A) [2.652(2) Å] and Se(1B)···N(1B) [2.628(2) Å] are much shorter than the related diselenides.[24,25] Although the distance is longer than the sum of the covalent radii (1.87 Å), these distances are significantly shorter than the sum of the van der Waals radii (3.5 Å). The most interesting feature of the structure is that the compound has crystallized in a chiral space group $P2_12_12_1$. Refinement of the Flack enantiopole parameter[26] led to a value of ~0 for **8**, thus confirming the enantiomeric purity of the crystals. The chirality of the compound may arise due to the strong Se···N interaction which can twist the whole molecule in such a way that it becomes chiral.

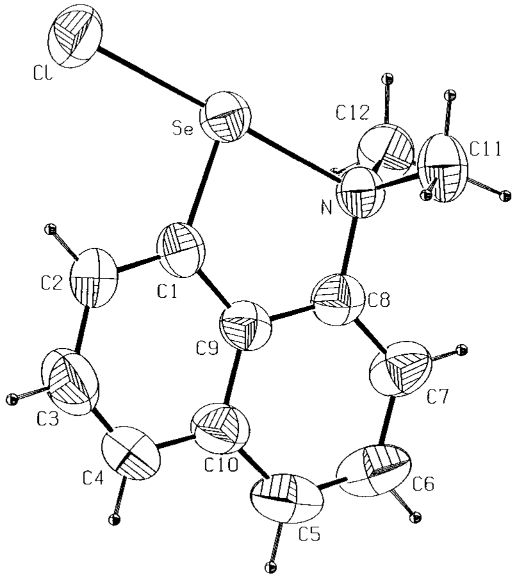

Figure 1. Crystal structure of compound **9**.

Molecular Structure of 9. An ORTEP view of compound **9** is shown in Figure 1. Significant bond lengths and angles are summarized in Table 2. The geometry around Se is T-shaped with selenium bonded to carbon, nitrogen, and chlorine. One of the shortest intramolecular nonbonded Se···N distances [Se···N 2.174(5) Å] was observed in this compound. This bond length is slightly less than the Se···N bond length [2.191(8) Å] in ArSeCl reported by Tomoda et al.,[4f] where the nitrogen is in sp^3 state and the Se···Cl bond is stereoelectronically stabilized by N···Se−Cl interaction. This bond length is also shorter than the one reported for a cationic species, chloro-substituted σ-am-

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Table 2. Significant Bond Lengths (Å) and Angles (deg) for 9

Se−C(1)	1.903(6)	Se−N	2.174(5)
Se−Cl	2.429(2)	N−C(8)	1.459(7)
N−C(12)	1.495(7)	N−C(11)	1.496(7)
C(1)−Se−N	83.2(2)	C(1)−Se−Cl	94.5(2)
N−Se−Cl	176.24(13)	C(8)−N−C(12)	112.24(13)
C(8)−N−C(11)	111.8(5)	C(12)−N−C(11)	110.6(5)
C(8)−N−Se	107.4(3)	C(12)−N−Se	108.1(4)
C(11)−N−Se	106.3(4)	C(2)−C(1)−Se	126.7(5)

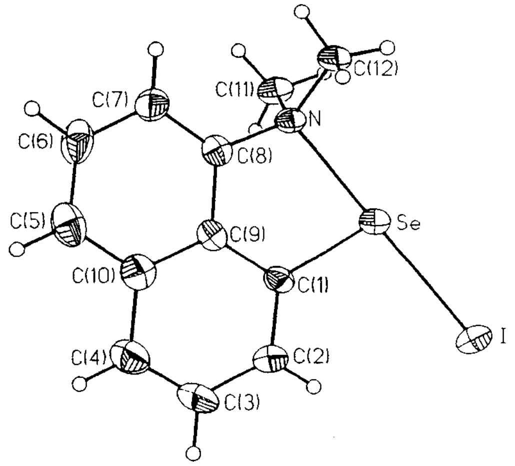

Figure 2. Crystal structure of compound **11**.

Table 3. Significant Bond Lengths (Å) and Angles (deg) for 11

Se−I	2.7419(9)	Se−C(1)	1.928(7)
Se−N	2.242(5)	N−C(8)	1.433(10)
N−C(11)	1.490(8)	N−C(12)	1.517(9)
C(1)−Se−N	82.1(3)	C(1)−Se−I	97.7(2)
N−Se−I	177.60(14)	C(8)−N−C(11)	112.2(6)
C(8)−N−C(12)	112.9(5)	C(11)−N−C(12)	110.2(6)
C(8)−N−Se	106.8(4)	C(11)−N−Se	106.9(4)
C(12)−N−Se	107.6(4)	C(2)−C(1)−Se	126.4(6)
C(9)−C(1)−Se	113.9(5)	C(7)−C(8)−N	124.8(7)
C(9)−C(8)−N	114.4(6)		

monioselenane, in which the Se···N bond length was 2.191 Å.[27] The Se−Cl bond length [2.429(2) Å] is much longer than the sum of their covalent radii (2.16 Å). This elongation in the Se−Cl bond can be easily explained in terms of N···Se−Cl interaction. The linear arrangement [N···Se−Cl 176.24(13)°] of the Se···Cl covalent bond and the nitrogen may allow an effective orbital interaction between the nitrogen lone pair and the σ^* orbital of the Se···Cl bond, resulting in the elongation of the Se−Cl bond.

Molecular Structure of 11. The molecular structure of **11** is shown in Figure 2. Table 3 gives the selected bond lengths and angles. Compound **11** is isostructural with **9**, which also crystallizes in a centrosymmetric space group with 8 molecules per unit cell. Compounds containing an Se−I bond are very rare, and only one RSeI compound has been characterized by X-ray crystallography, where the Se−I bond was stabilized by the sterically bulky 2,4,6-tri-*tert*-butylphenyl group.[19] In compound **11** the Se−I bond is strongly stabilized by Se···N nonbonded interaction. The Se···N distance, 2.242(5) Å, is longer than the single-bond covalent radii (1.87 Å) but considerably shorter than the sum of van der Waals radii (3.5 Å). As expected, the Se···N interaction lengthens the trans Se−I bond. The Se−I distance of 2.742(9) Å is ∼0.24 Å higher than the sum of covalent radii (2.50 Å) and also higher than that observed for 2,4,6,-tri-*tert*-butylphenyl(iodo)selenide [Se−I = 2.529(1) Å]. This clearly confirms that the Se···N interaction elongates the Se−I bond. The C(1)−Se−I bond angle 97.7(2)° is comparable to the C−Se−I bond angle reported for 2,4,6-tri-*tert*-butylphenyl(iodo)selenide [97.5(1)°]. The strong Se···N interaction leads to a nearly linear arrangement of the N···Se−I unit [∠N···Se−I 177.6°]. The Se−C(1) bond length, 1.928(7) Å, is comparable with other related compounds.[19]

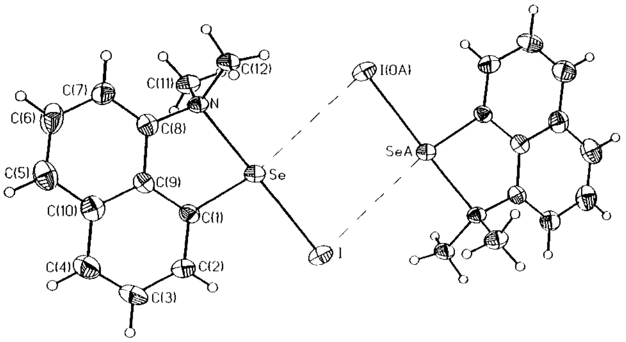

Figure 3. Crystal structure of compound **11** showing intermolecular Se···I interactions.

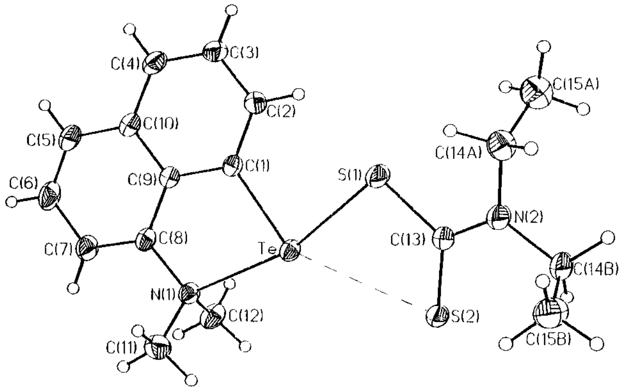

Figure 4. Crystal structure of compound **14**.

Of particular interest in this structure is the intermolecular interaction between two adjacent molecules (Figure 3). The molecules are linked into centrosymmetric dimers through weak intermolecular Se···I contacts. The interatomic distance between Se and I(0A) [4.033 Å] is greater than the sum of covalent radii (2.50 Å) but is within the van der Waals distance of 4.1 Å and therefore can be considered as a weak secondary interaction. Although this type of intermolecular interaction between Te and I is common in RTeI compounds, this is not very common in RSeI compounds. The chloro analogue (**9**) does not show any such intermolecular interactions.

Molecular Structure of 14. Compound **14** crystallizes in the space group $P2_1/c$. The ORTEP diagram is given in Figure 4. The bond lengths and angles are given in Table 4. The main feature of this structure is the presence of both Te···N and Te···S intramolecular nonbonded interactions. The coordination about tellurium can be considered as pseudo-trigonal bipyramidal. Although several Te(IV) complexes with dithiocarbamate ligands are known,[28] this complex is one of the rare examples of RTe(dtc) stabilized by intramolecular

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Table 4. Significant Bond Lengths (Å) and Angles (deg) for 14

Te−C(1)	2.131(3)	Te−N(1)	2.505(3)
Te−S(1)	2.5308(10)	S(1)−C(13)	1.759(3)
S(2)−C(13)	1.683(4)	N(1)−C(8)	1.456(4)
N(1)−C(12)	1.476(5)	N(1)−C(11)	1.479(5)
N(2)−C(13)	1.337(5)	N(2)−C(14B)	1.467(5)
N(2)−C(14A)	1.510(5)	C(1)−Te−N(1)	75.84(11)
C(1)−Te−S(1)	89.57(9)	N(1)−Te−S(1)	164.28(7)
C(13)−S(1)−Te	99.70(12)	C(8)−N(1)−C(12)	111.0(3)
C(8)−N(1)−C(11)	113.3(3)	C(12)−N(1)−C(11)	109.6(4)
C(8)−N(1)−Te	106.9(2)	C(12)−N(1)−Te	107.3(2)
C(11)−N(1)−Te	108.5(2)	C(13)−N(2)−C(14B)	121.1(3)
C(13)−N(2)−C(14A)	123.9(3)	C(14B)−N(2)−C(14A)	114.6(3)
C(2)−C(1)−Te	123.8(2)	C(9)−C(1)−Te	116.7(2)
C(7)−C(8)−N(1)	121.5(3)	C(9)−C(8)−N(1)	116.9(3)
N(2)−C(13)−S(2)	124.0(3)	N(2)−C(13)−S(1)	115.0(3)
S(2)−C(13)−S(1)	121.0(2)	C(15A)−C(14A)−N(2)	110.0(4)
N(2)−C(14B)−C(15B)	111.8(4)		

coordination.[29] The Te⋯N bond length of 2.505 (4) Å seems to be quite strong compared with the Te⋯N bond lengths observed in the corresponding ditelluride [2.743(5) and 2.699(5) Å].[6d] This difference is due to the bonding of the more electronegative dithiocarbamate ligand to tellurium. The dithiocarbomate is unsymmetrical. The long and short C−S bonds are 1.759(3) and 1.683(4) Å, respectively. The corresponding Te−S bond lengths are accordingly long and short. (Te−S(1) = 2.531(10) Å and Te−S(2) = 3.246(10) Å). The short Te−S bond is roughly trans to the Te−N bond [∠N⋯Te−S 164.3(4)°]. A kind of trans influence relating the strength of the Te−S bond to the Te−N bond is observed in this case, as the Te−S distance of 2.531(10) Å is greater than the sum of the covalent radii of Te and S (2.41 Å). The Te−S(2) bond is considered to be weak, but the bond length of 3.246(10) Å is much less than the sum of the van der Waals radii of Te and S (3.7Å). The Te−S(1) bond length of 2.531(10) Å is comparable to the Te−S bond length in dimethyldithiocarbomato-[2-(2-pyridyl)phenyl]tellurium(II),[29b] PhTe(Et_2NCS_2)$_2$I,[30] and [NEt_4][Te(S_2CNEt_2)$_2$]$_2$[31] complexes (2.551−2.564 Å). The angle subtended at Te between the two sulfurs is 61.0°, whereas that between carbon and nitrogen is 75.8°. The sum of the four angles at tellurium is 360°, indicating that the atoms Te, S(1), S(2), C(1), and N(1) are almost in a plane. Hence the geometry around tellurium is better described as planer trapezoidal. The Te−C(1) bond length of 2.131(3) Å is comparable with the Te−C (aliphatic) bonds (2.125−2.139 Å).[32] The same phenomenon was noted in a comparison of the structure of $Me_2Te(S_2CNMe_2)_2$[32] with that of its $Ph_2Te[S_2NR_2]_2$ analogues[32] and suggests a relatively stronger Te−C (methyl) bond than might be anticipated in view of the fact that Te−C (aromatic) bonds are generally stronger than Te−C (aliphatic) bonds. This also suggests that the nature of the organic group in the dithiocarbamate complexes appears to have little effect, whereas the intramolecular Te⋯N interaction alters the Te⋯S bond lengths. There is no significant secondary Te⋯S intermolecular interaction.

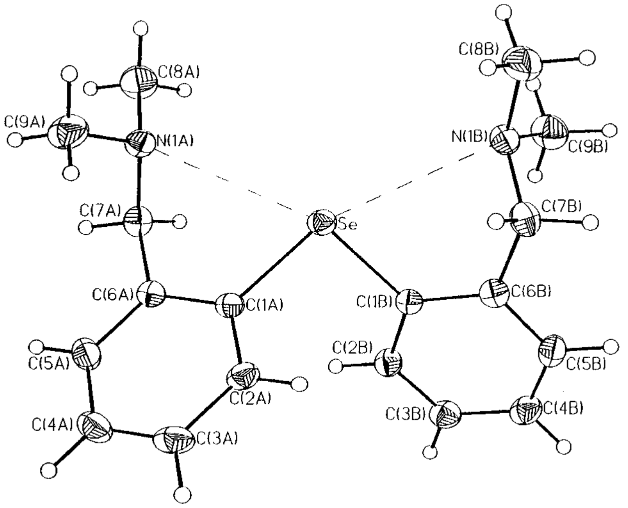

Figure 5. Crystal structure of compound **18**.

Table 5. Significant Bond Lengths (Å) and Angles (deg) for 18

Se−C(1B)	1.935(3)	Se−C(1A)	1.941(3)
N(1A)−C(9A)	1.443(5)	N(1A)−C(7A)	1.453(4)
N(1A)−C(8A)	1.460(4)	N(1B)−C(9B)	1.453(5)
N(1B)−C(8B)	1.453(5)	N(1B)−C(7B)	1.458(4)
C(1B)−Se−C(1A)	96.77(12)	C(9A)−N(1A)−C(7A)	112.0(3)
C(9A)−N(1A)−C(8A)	110.6(3)	C(7A)−N(1A)−C(8A)	109.4(3)
C(9B)−N(1B)−C(8B)	110.8(3)	C(9B)−N(1B)−C(7B)	112.6(3)
C(8B)−N(1B)−C(7B)	110.8(3)	C(2A)−C(1A)−Se	119.3(2)
C(6A)−C(1A)−Se	120.4(2)	N(1A)−C(7A)−C(6A)	112.7(3)
C(2B)−C(1B)−Se	119.4(2)	C(6B)−C(1B)−Se	121.0(2)
N(1B)−C(7B)−C(6B)	112.1(3)		

Molecular Structure of 18. An ORTEP[33] view of **18** is shown in Figure 5. The selected bond lengths and angles are given in Table 5. The structure shows **18** as a discrete monomer with four molecules per unit cell. This is isostructural with the tellurium analogue, R_2Te (**19**).[6c] The bond configuration about the Se atom is V-shaped, and the angle C(1A)−Se−C(1B) is 96.77(12)°. Owing to the presence of two monodentate N-donor atoms and the possibility of intramolecular coordination with the Se atom, it is possible that either one or both Se⋯N coordination bonds may be formed. A look at the structure shows that the N(1A) and N(1B) atoms form the characteristic envelop over the Se atom, which would facilitate the formation of the five-membered rings (cis-conformation). Similar to the tellurium analogue,[6c] the two Se⋯N distances [Se⋯N(1A) = 3.190 Å, Se⋯N(1B) = 3.099 Å] are not identical. The Se⋯N(1B) interaction is stronger than the Se⋯N(1A). Further, the average Se⋯N distance of 3.145 Å is much longer compared with the average Se⋯N distance in the corresponding diselenide.[2c] However, these Se⋯N bond lengths are well within the sum of van der Waals radii of Se and N (3.5 Å) and probably represent a weak but significant interaction. The average Se⋯N distance of

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3.145 Å is 0.355 Å shorter than the Se···N van der Waals distance (3.5 Å), whereas for the tellurium analogue the average Te···N distance of 3.097 Å was about 0.603 Å shorter than the Te···N van der Waals distance (3.7 Å). This further indicates that the Te···N interactions are, in general, much stronger than the Se···N distances in related compounds. This is not surprising because it is known that the hypervalent property of divalent chalcogens increases in the order O < S < Se < Te.[4e] The Se−C(1A) and Se−C(1B) bond lengths of 1.941(3) and 1.935(3) Å, respectively, are in agreement with the value of 1.93 Å suggested by Pauling[22] and typical values for other related diselenides.[24,25]

Conclusions

A comparison of structure and reactivity among intramolecularly coordinated low-valent organochalcogen complexes derived from *N*,*N*-dimethylnaphthylamine and *N*,*N*-dimethylbenzylamine has been made. It is found that the stability and reactivity of the compounds mainly depend on the strength of the E···N (E = Se, Te) interaction and the steric bulkiness of the ligand. The more rigid naphthylamine-based ligand shows different reactivity and bonding properties compared with the more flexible *N*,*N*-dimethylbenzylamine-based ligand. These include following: (i) The chalcogenides, R_2E, could not be isolated in the case of **4**, whereas **1** afforded the chalcogenides in excellent yield. (ii) The reactions of the lithiated compound derived from *N*,*N*-dimethylnaphthylamine with $Te(dtc)_2$ or TeI_2, however, afforded RTe(dtc) or RTeI. (iii) The strength of Se···N or Te···N nonbonded interactions in *N*,*N*-dimethylnaphthylamine-based compounds is much stronger than those derived from *N*,*N*-dimethylbenzylamine. (iv) The diselenide and ditelluride[6d] derived from *N*,*N*-dimethylnaphthylamine are chiral, whereas the diselenide[3d] and ditelluride[6c] derived from *N*,*N*-dimethylbenzylamine are not chiral. The E···N (E = Se, Te) intramolecular interactions in both the cases alter the bond lengths of E−X (X = Se, I, S) due to its trans influence.

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Supporting Information Available: The complete tables of crystallographic data, final atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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