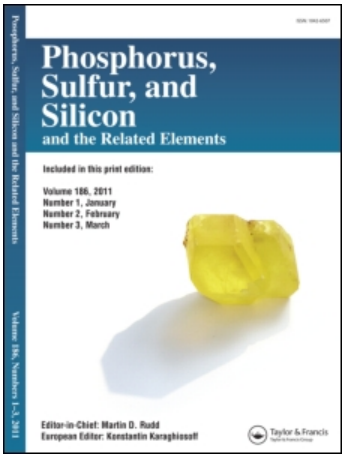

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THIURAMDISELENIDES

Wolfgang Dietzsch[a]; Joachim Sieler[a]; Wolfgang Meiler[a]; Wolfgang Robien[a]
[a] Department of Chemistry and Physics and Institute of Organic Chemistry, University of Vienna, Vienna, Austria

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THIURAMDISELENIDES

WOLFGANG DIETZSCH, JOACHIM SIELER, WOLFGANG MEILER
Department of Chemistry and Physics and
WOLFGANG ROBIEN
Institute of Organic Chemistry, University of Vienna,
1090 Vienna, Austria

Abstract The oxidation products of thioseleno-carbamate ions R_2NCSSe^- are, in contrast with the homologous selenuramdiselenides, stable red, highly crystalline diselenides (R_2N = Et_2N, morpholyl, pyrrolidyl, Bz_2N) or yellow (cyclohexyl$_2$N). The ^{77}Se NMR spectra show one signal with chemical shifts between 1060 and 1125 ppm (referenced to Ph_3PSe). The x-ray structures of the tetraethyl (I) and tetracyclohexyl (II) compounds show unexpected differences. Whereas (I) contains an inversion center bisecting a planar NC(S)Se-Se(S)CN unit, we found for (II) a dihedral angle of 80.4 between two very different cyclohexyl$_2$ halves: S(1)-C(1)-Se(1) = 103.0° and S(2)-C(2)-Se(2) = 119.1°, respectively.

INTRODUCTION

Dithiocarbamate, thioselenocarbamate and diselenocarbamate ions $R_2NCX_2^-$ (X = S and/or Se) are readily oxidized, e.g., by air[1] or hydrogen peroxide[2] in suitable solvents. Whereas the oxidation products of dithiocarbamates are always the corresponding thiuramdisulfides, the diselenuramdiselenides formed initially from the diselenocarbamates disproportionate into a 1:1 mixture of monoselenide $(R_2NCSe)_2Se$ and "triselenides" $(R_2NCSe)_2Se_3$[3]. X-ray single crystal analysis shows that the latter products are in reality bis(diselenocarbamato)selenium(II) complexes, $(R_2NCSe_2)_2Se$[4].

In 1938 Scott[5] proposed that the oxidation products of thioselenocarbamates are thiuramdiselenides[5]. This was confirmed

in 1974 by ESCA experiments[1b]. The surprising stabilities of thiuramdiselenides in contrast with selenuramdiselenides led us to carry out x-ray analyses on the brick-red tetraethyl and the yellow tetracyclohexyl compounds.

EXPERIMENTAL

The compounds were obtained as described by Heber, et al.[6] ^{77}Se NMR spectra of saturated $CDCl_3$ solutions were recorded on a BRUKER WM-250 spectrometer operating at 47.75 MHz[7]. Structural data were collected on a CAD-4 diffractometer.

TABLE I Crystal data collection summary.

	Compound (I)	(II)
Formula	$C_{10}H_{20}N_2S_2Se_2$	$C_{26}H_{44}N_2S_2Se_2$
Molecular weight	390.3	606.7
Space group	$P2_1/c$	$P2_1/n$
a(Å)	6.384(1)	10.461(3)
b(Å)	11.180(3)	18.141(11)
c(Å)	11.480(2)	15.224(7)
β(°)	103.51(2)	95.15(3)
Volume ($Å^3$)	796.7	2877.6
Temperature (°C)	24	24
$D_{calcd.}$ ($g \cdot cm^{-3}$)	1.63	1.40
Z	2	4
μ(MoK) (cm^{-1})	49.1	29.1
Size of crystals (mm)	0.3x0.2x0.15	0.2x0.2x0.3
Color	brick-red	yellow
Scan method	ω/2θ	ω/2θ
Range of data (deg.)	$3 \leq 2\theta \leq 56$	$3 \leq 2\theta \leq 56$
No. of reflections	2216	4155

Continuation of Table I

	Compound (I)	(II)
No. of reflections with $F>2\sigma\|F\|$	1190	3231
$R_{aniso.}$	0.040	0.059

RESULTS AND DISCUSSION

The properties and ^{77}Se NMR data of the prepared thiuramdiselenides are summarized in Table II.

TABLE II Properties and ^{77}Se NMR chemical shifts of the diselenides $(R_2NC(S)Se^-)_2$

R_2N	Melting point (°C)	Color	$\delta(^{77}Se)$ (ppm/Ph_3PSe)
Et_2N	85-86	brick-red	1096.5
Morpholyl	133-134	brick-red	1063.0
Pyrrolidyl	154-155	brick-red	1060.1
Bz_2N	124-125	orange	1122.1
$cHex_2N$	178-182	yellow	1089.3

The molecular geometries and atom numbering of both molecules (I) and (II) are shown in Figures 1 and 2. Selected bond distances and angles are given in Table IV. As can be seen there exist significant differences between the two structures. The tetraethyl compound contains a planar C(S)Se-Se'(S')C' trans arrangement and the whole molecule has an inversion center which bisects the Se-Se' axis. This is in contrast to the structures of thiuramdisulfides that exhibit torsion angles near 90° about the S-S' vector of the disulfide bond[1a,8]. Such an angle, however, is also found in the tetracyclohexylthiuramdiselenide. Moreover, this molecule consists of two totally different halves:

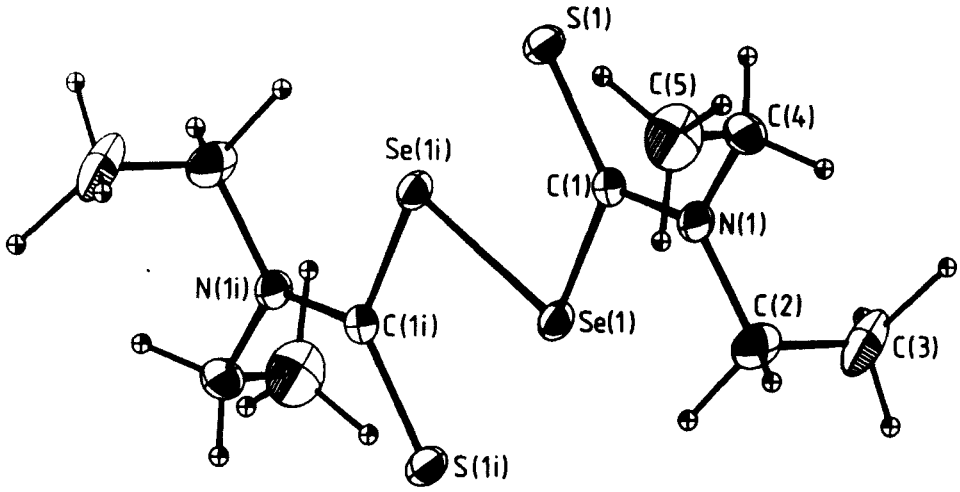

FIGURE 1 Geometry of tetraethyl thiuramdiselenide (I).

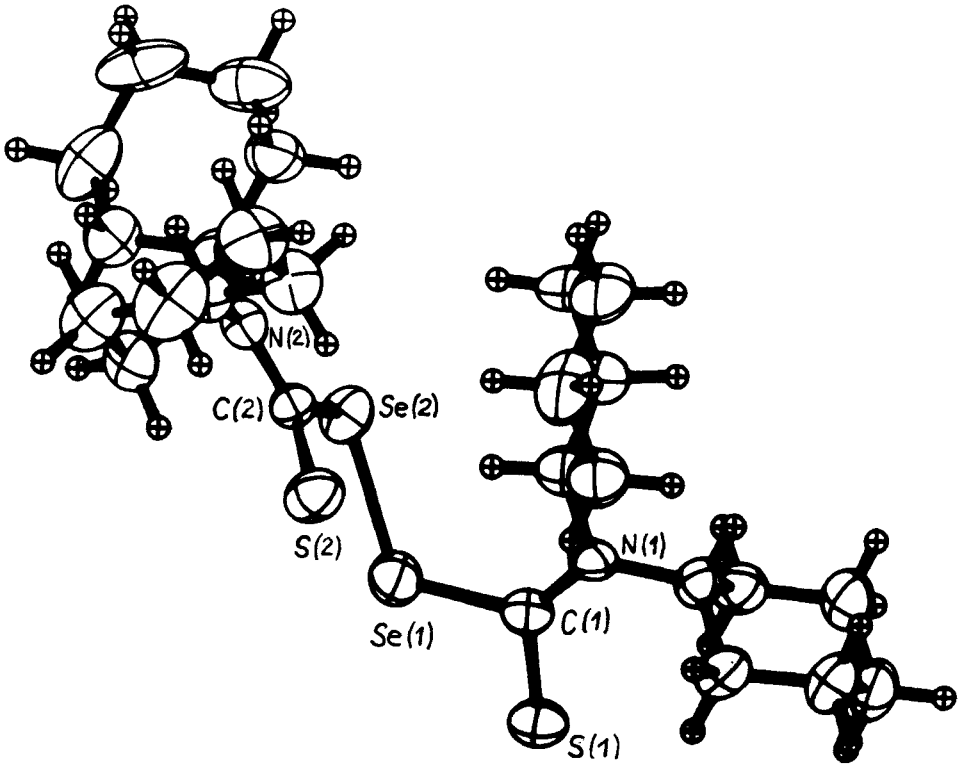

FIGURE 2 Geometry of tetracyclohexyl thiuramdiselenide (II).

TABLE III Fractional coordinates and temperature factors.

Compound (I)

Atom	x	y	z	B
Se(1)	.9152(1)	.07081(6)	.04874(6)	4.35(3)
S(1)	1.4136(3)	.0534(2)	.1547(2)	4.90(7)
N(1)	1.1592(8)	.2068(5)	.2314(5)	3.5(2)
C(1)	1.1835(9)	.1202(5)	.1581(6)	3.7(2)
C(2)	.953(1)	.2695(8)	.2265(8)	5.1(3)
C(3)	.928(2)	.3777(10)	.1488(12)	6.9(4)
C(4)	1.345(1)	.2544(8)	.3215(9)	5.2(3)
C(5)	1.383(2)	.1833(11)	.4365(11)	7.0(3)
H(21)	.928(8)	.285(5)	.310(4)	8.6(5)
H(22)	.821(11)	.202(6)	.208(5)	8.8(5)
H(31)	1.068(15)	.456(8)	.177(7)	9.7(6)
H(32)	.792(15)	.407(7)	.151(7)	9.8(6)
H(33)	.931(10)	.373(9)	.071(8)	9.6(6)
H(41)	1.298(10)	.334(6)	.340(6)	8.7(5)
H(42)	1.458(9)	.255(5)	.287(5)	8.9(6)
H(51)	1.235(17)	.171(9)	.486(8)	9.8(6)
H(52)	1.472(14)	.111(8)	.414(7)	10.1(7)
H(53)	1.461(14)	.227(8)	.494(8)	10.2(8)

Compound (II)

Atom	x	y	z	B
Se(1)	.08041(8)	.07794(5)	.60465(6)	4.68(3)
Se(2)	.15450(8)	-.04423(5)	.61422(6)	4.35(3)
S(1)	-.1173(2)	.1843(1)	.5910(2)	5.23(8)
S(2)	.2180(2)	.0178(1)	.8054(1)	4.90(7)
N(1)	-.1703(5)	.0581(3)	.6748(4)	3.5(2)
N(2)	.3119(5)	-.1101(3)	.7512(4)	3.4(2)
C(1)	-.0914(7)	.0996(4)	.6329(5)	3.7(2)
C(2)	.2420(6)	-.0492(4)	.7340(5)	3.3(2)
C(3)	-.3117(6)	.0726(4)	.6755(5)	3.7(2)
C(4)	-.3786(7)	.0756(4)	.5810(5)	4.6(3)
C(5)	-.5238(7)	.0819(5)	.5853(5)	4.9(3)
C(6)	-.5569(7)	.1503(5)	.6407(6)	5.2(3)
C(7)	-.4885(7)	.1461(5)	.7324(5)	4.2(3)
C(8)	-.3420(7)	.1411(4)	.7293(5)	4.3(3)
C(9)	-.1218(7)	-.0080(4)	.7249(5)	4.4(3)
C(10)	-.1534(7)	-.0036(5)	.8216(5)	5.5(3)
C(11)	-.0992(8)	-.0713(5)	.8730(6)	7.0(3)
C(12)	-.1486(8)	-.1436(5)	.8298(7)	7.9(3)
C(13)	-.1174(8)	-.1467(5)	.7339(7)	6.9(4)

Continuation of Table III - Compound (II)

Atom	x	y	z	B
C(14)	-.1719(7)	-.0793(4)	.6821(5)	5.1(3)
C(15)	.3706(6)	-.1311(4)	.8403(5)	4.0(3)
C(16)	.2716(7)	-.1436(5)	.9070(5)	5.3(3)
C(17)	.3368(8)	-.1747(5)	.9923(6)	6.7(3)
C(18)	.4458(9)	-.1251(5)	1.0295(5)	7.5(4)
C(19)	.5409(8)	-.1110(5)	.9635(5)	6.1(3)
C(20)	.4761(7)	-.0787(5)	.8774(5)	4.6(3)
C(21)	.3368(7)	-.1644(4)	.6807(5)	3.9(2)
C(22)	.2719(7)	-.2383(5)	.6934(5)	5.3(2)
C(23)	.2994(9)	-.2917(5)	.6202(6)	7.2(4)
C(24)	.442(1)	-.3036(5)	.6164(6)	7.7(4)
C(25)	.5067(8)	-.2282(5)	.6021(6)	7.0(3)
C(26)	.4803(7)	-.1730(5)	.6743(5)	5.4(3)

TABLE IV Selected distances (Å) and angles (°).

Compound (I)

Se(1)-Se(1')	2.345(1)		
Se(1)-C(1)	1.952(5)		
S(1)-C(1)	1.656(6)		
Se(1)-S(1)	3.136(1)		
N(1)-C(1)	1.316(8)		
N(1)-C(2)	1.482(9)		
N(1)-C(4)	1.479(9)		
Se(1)- C(1)- S(1)	120.5(4)		
Se(1')-Se(1)- C(1)	93.7(2)		
N(1) - C(1)-Se(1)	113.8(4)		
N(1) - C(1)- S(1)	125.7(4)		
C(2) - N(1)- C(4)	114.7(6)		
C(1) - N(1)- C(2)	124.0(5)		
C(1) - N(1)- C(4)	121.1(6)		

Compound (II)

Se(1)-Se(2)	2.348(2)		
Se(1)- C(1)	1.926(7)	Se(2)- C(2)	1.968(7)
S(1)- C(1)	1.676(7)	S(2)- C(2)	1.665(7)
S(1)-Se(1)	2.822(3)	S(2)-Se(2)	3.135(2)
N(1)- C(1)	1.323(9)	N(2)- C(2)	1.338(9)
N(1)- C(3)	1.503(8)	N(2)-C(15)	1.487(9)
N(1)- C(9)	1.503(8)	N(2)-C(21)	1.497(9)

Continuation of Table IV - Compound II)

Se(1)- C(1)- S(1)	103.0(4)
Se(2)-Se(1)- C(1)	119.2(2)
N(1)- C(1)-Se(1)	128.8(5)
N(1)- C(1)- S(1)	128.2(6)
C(3)- N(1)- C(9)	115.4(5)
C(1)- N(1)- C(9)	120.5(6)
C(1)- N(1)- C(3)	124.1(6)
Se(2)- C(2)- S(2)	119.1(4)
Se(1)-Se(2)- C(2)	103.0(2)
N(2)- C(2)-Se(2)	114.8(5)
N(2)- C(2)- S(2)	125.9(5)
C(15)- N(2)-C(21)	113.7(5)
C(2)- N(2)-C(21)	122.0(6)
C(2)- N(2)-C(15)	124.3(6)

Se(1)-C(1)-S(1) 103.0(4)° and Se(2)-C(2)-S(2) 119.1(4)°. The Se-C bond lengths also differ remarkably (1.926(7) and 1.968(7)Å, respectively). The very broad ^{77}Se NMR signal (320 Hz) of this compound shows that differences exist in solution between this yellow compound and the red ones.

No significant differences are observed between tetraethyl thiuramdiselenide, tetraethyl thiuramdisulfide[8c], or bis(diethyldiselenocarbamato)selenium(II)[4] with respect to the $(H_5C_2)_2NC$ part of the molecules. The double bond character of the terminal C-S bonds seems to be somewhat lower in the diselenides, inverse to the very small differences in the C(1)-N(1) (or C(2)-N(2)) distances.

The Se-Se bond lengths are similar in size to those reported in other diselenides, e.g., di-p-chlorobenzene diselenide (2.333 Å)[9], Na_2Se_2 (2.38 Å)[10], or 1,2-diselenane-3,6-dicarboxylic acid (2.32 Å).[11]

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