

The crystal and molecular structure of bis(piperidinyldithiocarbamato)selenium(II)

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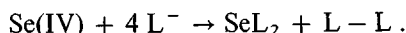
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Bis(piperidinyldithiocarbamato)selenium(II) | Crystal structure

Abstract. Selenium(IV) undergoes reductive complexation with dithiocarbamate ($R_1^R_2 > N - CS_2^- = L^-$) to give SeL_2 . The complexes prepared are with $R_1 = R_2 = n$ -propyl, isopropyl and $R_1R_2N =$ piperidinyldiyl. The crystal structure of bis(piperidinyldithiocarbamato)selenium(II) is reported. The crystals are monoclinic, space group $P2_1/n$ with cell parameters $a = 8.735(1)$, $b = 11.530(2)$, $c = 16.766(3)$ Å, $\beta = 100.58(1)^\circ$, $F(000) = 816$. Final $R = 0.088$ for 2879 unique reflections. The SeS_4 core has a planar trapezoidal configuration. The dithiocarbamate ligands are present as unequal bidentates with one short Se–S [2.301(3) Å] and long Se–S [2.785(3) Å] bonds. The average Se–S bond distance 2.547(4) Å is close to the average Se–S distance observed in four coordinated Se(II)–sulphur ligand complexes.

Introduction

Selenium(IV) undergoes reductive complexation with dithiocarbamates (L^-) to give the corresponding selenium(II) complex (SeL_2) and the thiramdisulphide ($L-L$)



In the literature, only two SeL_2 complexes have been reported, with $R_1 = R_2 =$ ethyl (Husebye and Madsen, 1970) and $R_1R_2N =$ morpholyl

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(Anderson and Husebye, 1970). The crystal structures of these complexes were solved using multiple film data and the complexes were also found to be not very stable. In an attempt to prepare stabler selenium(II)dithiocarbamate complexes, dithiocarbamates with varied substituents such as $R_1 = R_2 = n$ -propyl and isopropyl, $R_1R_2N =$ piperidinyl are interacted with selenium(IV). These complexes are indefinitely stable in solid state. The crystal structure of bis(piperidinyl-dithiocarbamato)selenium(II) is determined.

Experimental

Preparation of the complexes

1 mmol of selenium dioxide (0.111 g) dissolved in 10 ml of methanol was mixed with 6 mmol (a g of anhydrous salt) (when $R_1 = R_2 = n$ -propyl or isopropyl $a = 1.194$ g; $R_1R_2N =$ piperidinyl, $a = 1.098$ g) of the sodium salt of the dithiocarbamate ($\text{NaL} \cdot x \text{H}_2\text{O}$) dissolved in 30 ml of water and 10 ml of 4N hydrochloric acid. The yellow precipitate formed, which was a mixture of SeL_2 and L-L, was washed with 5 ml of ether. Fractional crystallization from dichloromethane-carbon tetrachloride gave pure SeL_2 complexes (yield: 88–93% in the initial crops). Single crystals, suitable for crystal work were obtained by recrystallizing the complex from dichloromethane-ethylacetate solvent mixture.

Crystal data of bis(piperidinyl)dithiocarbamato)selenium(II)



A single crystal of size 0.67 mm \times 0.12 mm \times 0.65 mm was chosen under polarising microscope and mounted on an Enraf-Nonius CAD4 diffractometer. CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$) obtained with a graphite monochromator was used in the $\omega/2\theta$ scan mode. Unit-cell parameters were obtained from least-squares refinement of θ values of 25 high angle reflections. 3411 total reflections were collected in the range $2 \leq \theta \leq 70^\circ$ ($-10 \leq h \leq 10, 0 \leq K \leq 14, 0 \leq l \leq 20$), out of which 2612 reflections satisfied $I \geq 3\sigma(I)$. No significant variation was observed in the intensities of two check reflections [(45 $\bar{1}0$) and (27 $\bar{8}$)] which were measured every hour of X-ray exposure. $\mu(\text{CuK}_\alpha)$ was calculated to be 73.45 mm^{-1} . Absorption correction was applied and structure solved by the heavy-atom method using SHELX-76 (Sheldrick, 1976) program. Atomic scattering factors for non-hydrogen atoms were taken from Cromer and Mann (1968) and the anomalous dispersion correction factor as applied to all the non-hydrogen atoms were taken from Cromer and Libermann (1970). The hydrogen scattering factors were taken from Stewart et al. (1965). All the non-hydrogen atoms were refined with anisotropic thermal parameters. All the

hydrogen atoms except one appeared in difference Fourier maps and were refined isotropically. The final R and R_w values are 0.088 and 0.104 respectively ($w = 1/[\sigma^2(F) + 1.2401|F|^2]$). The final difference Fourier map was featureless.

Results and discussion

Final fractional atomic coordinates are given in Table 1. In Table 2 are presented the bond lengths and bond angles involving the non-hydrogen atoms. Figure 1 depicts the ORTEP (Johnson, 1965) plot of the molecule.¹

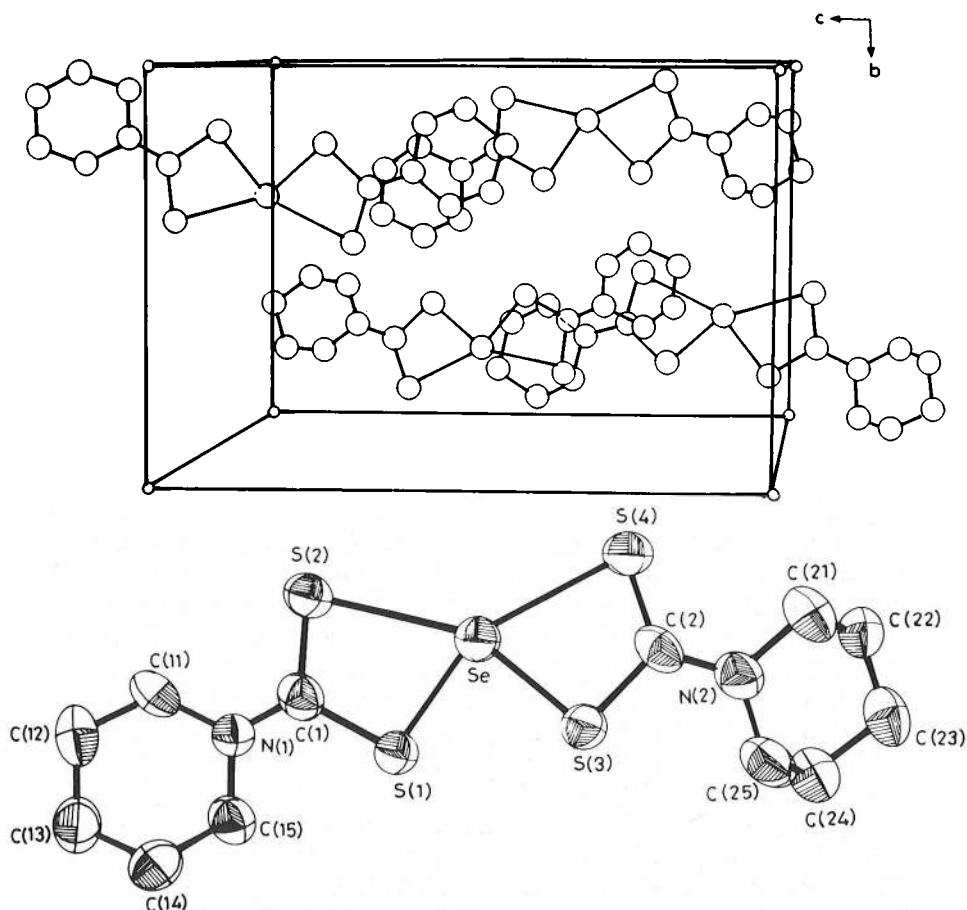


Fig. 1. Perspective view of the molecule.

¹ Additional material to this paper can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 52548, the names of the authors and the title of the paper.

Table 1. Fractional atomic coordinate and U_{eq} with standard deviations in parentheses,

$$U_{eq} = \frac{1}{3} \sum_{i=1}^3 U_{ii}.$$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Se	0.1253(1)	0.1625(1)	0.6135(1)	0.0601(5)
S(1)	0.1319(3)	0.3244(2)	0.5339(1)	0.0651(14)
S(2)	0.1200(3)	0.0971(2)	0.4531(1)	0.0683(14)
S(3)	0.1376(3)	0.2941(2)	0.7174(1)	0.0651(14)
S(4)	0.1302(3)	0.0480(2)	0.7616(2)	0.0723(16)
C(1)	0.1195(10)	0.2444(8)	0.4432(5)	0.061(5)
C(2)	0.1449(9)	0.1877(7)	0.7922(6)	0.062(4)
C(11)	0.0817(13)	0.2399(9)	0.2946(5)	0.077(6)
C(12)	0.1880(13)	0.2873(10)	0.2426(7)	0.081(6)
C(13)	0.1670(14)	0.4179(9)	0.2321(6)	0.087(8)
C(14)	0.1912(10)	0.4755(8)	0.3120(6)	0.076(5)
C(15)	0.0895(12)	0.4276(9)	0.3665(7)	0.079(6)
C(21)	0.1764(13)	0.1419(10)	0.9344(6)	0.081(7)
C(22)	0.0570(12)	0.1723(10)	0.9880(6)	0.072(5)
C(23)	0.0677(11)	0.2977(10)	1.0131(6)	0.080(5)
C(24)	0.0648(10)	0.3793(8)	0.9409(5)	0.070(5)
C(25)	0.1843(13)	0.3452(8)	0.8916(6)	0.082(4)
N(1)	0.1064(9)	0.2990(6)	0.3736(5)	0.068(4)
N(2)	0.1681(9)	0.2236(7)	0.8681(4)	0.071(4)

Table 2. Some important bond lengths (Å) and bond angles (°) and their standard deviations in parentheses.

Atoms	Bond length	Atoms	Bond length
Se–S(1)	2.301(3)	Se–S(2)	2.785(3)
Se–S(3)	2.298(3)	Se–S(4)	2.805(4)
S(1)–C(1)	1.766(9)	S(2)–C(1)	1.706(10)
C(1)–N(1)	1.311(11)	N(1)–C(11)	1.470(12)
C(11)–C(12)	1.489(16)	C(12)–C(13)	1.523(15)
C(13)–C(14)	1.475(14)	C(14)–C(15)	1.492(15)
C(15)–N(1)	1.493(12)	S(3)–C(2)	1.747(9)
S(4)–C(2)	1.688(8)	C(2)–N(2)	1.318(12)
N(2)–C(21)	1.448(13)	C(21)–C(22)	1.537(16)
C(22)–C(23)	1.504(16)	C(13)–C(24)	1.531(14)
C(24)–C(25)	1.500(12)	C(25)–N(2)	1.457(12)
S(1)–Se–S(2)	70.0(2)	S(3)–Se–S(4)	69.4(2)
S(1)–Se–S(3)	84.3(2)	S(2)–Se–S(4)	136.2(3)
S(1)–C(1)–S(2)	115.9(5)	S(1)–C(1)–N(1)	119.8(6)
S(2)–C(1)–N(1)	124.3(6)	C(1)–N(1)–C(11)	123.6(6)
N(1)–C(11)–C(12)	110.7(7)	C(11)–C(12)–C(13)	110.8(8)
C(12)–C(13)–C(14)	110.2(8)	C(13)–C(14)–C(15)	112.8(7)
C(14)–C(15)–N(1)	110.8(7)	C(15)–N(1)–C(1)	122.6(6)
S(3)–C(2)–S(4)	117.5(6)	S(3)–C(2)–N(2)	116.8(6)
S(4)–C(2)–N(2)	125.6(6)	C(2)–N(2)–C(21)	120.9(7)
N(2)–C(21)–C(22)	110.9(8)	C(21)–C(22)–C(23)	111.6(8)
C(22)–C(23)–C(24)	112.2(8)	C(23)–C(24)–C(25)	111.3(7)
C(24)–C(25)–N(2)	111.0(7)	C(25)–N(2)–C(2)	123.6(7)

Table 3. Bond lengths and angles of some sulphur ligated selenium(II) complexes.

Complex	M–S (Å)	Average M–S (Å)	S–M–S (°)	Reference
Se(morphdtc) ₂	2.298(6) 2.786(6)	2.542(6)	70.5(2) 84.6(2) 69.7(2) 135.0(2)	Anderson and Husebye (1970)
Se[(C ₂ H ₅) ₂ NCS ₂] ₂	2.322(14) 2.75(4)	2.536(27)	70.9(2) 87.7(2) 70.9(2) 131.5(2)	Husebye and Madsen (1970)
Se[N(Ph ₂ PS) ₂] ₂	2.267(1) 3.001(1)	2.634(1)	84.14(4) 98.06(5) 94.99(5) 83.83(5)	Husebye and Moe (1983)
Se(CH ₃ OCS ₂) ₂	2.170(9) 2.205(6)	2.188(7)	80.0(2) 87.6(2) 91.2(2) 100.8(3)	Brondmo et al. (1975)
Se(Ptu) ₄ Cl ₂ · 2HCl	2.525(6) 2.543(6)	2.534(6)	89.1(2)	Sowrirajan et al. (1985)
Se ₂ (Ptu) ₆ Br ₄ 10H ₂ O	2.296(4) 2.846(4)	2.571(4)	89.9(2) 97.6(2) 87.6(2) 85.0(2)	Chidambaram et al. (1986)
Se(pipdtc) ₂	2.299(3) 2.795(4)	2.547(4)	70.0(2) 84.3(2) 69.4(2) 136.2(3)	Present study

than the sum of single covalent bond radii of selenium and sulphur of 2.11 Å. The longer Se–S bonds are weak covalent bonds and are much shorter than the sum of the van der Waals radii 3.78 Å. In Table 3 are presented the relevant data available regarding four-coordinated selenium(II)–sulphur ligand complexes. In all the 1,1-dithio ligand complexes, selenium(II) essentially exhibits planar trapezoidal geometry. In monodentate ligands (complexes 5 and 6) selenium(II) shows trapezoidal or square planar arrangement for bridging or all terminal ligand complexes respectively.

There are two different sets of C–S bond distances in each ligand, 1.766, 1.706, 1.747, 1.688 Å with average 1.723(9) Å. This is shorter than the sum of single covalent radii of C–S, 1.81 Å. Exclusively the longer C–S bond distance corresponds to the sulphur which is more strongly bonded

to selenium. The average C—N bond distance of 1.314(11) Å is significantly shorter than the sum of single bond radii 1.47 Å. These facts support the existence of the canonical form B. All the N—C and C—C bond distances and bond angles are normal. No abnormal short contacts in the structure are observed.

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