Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.913$, $T_{\max} = 0.983$
11 799 measured reflections
3688 independent reflections
2555 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.072$
$\theta_{\max} = 28.28°$
$h = -7 \rightarrow 7$
$k = -22 \rightarrow 37$
$l = -13 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.165$
$S = 1.056$
3688 reflections
221 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0958P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.314$ e Å^{-3}
$\Delta\rho_{\min} = -0.396$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

S1—C8	1.667 (2)	N1—C8	1.391 (2)
O1—C7	1.233 (2)	N2—C8	1.330 (2)
N1—C7	1.380 (2)	N2—C9	1.423 (2)
C7—N1—C8	128.2 (2)	O1—C7—C1	121.7 (2)
C8—N2—C9	127.9 (2)	N2—C8—N1	115.6 (2)

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
N2—H1N2$\cdots$O1	0.80 (2)	1.92 (2)	2.619 (2)	145 (2)
C10—H10$\cdots$S1	0.95 (2)	2.85 (2)	3.253 (2)	107 (2)
N1—H1N1$\cdots$S1$^{\rm i}$	0.83 (2)	2.70 (2)	3.501 (2)	163 (3)

Symmetry code: (i) $1 - x, 1 - y, 2 - z$.

For both compounds, data collection: *SMART* (Siemens, 1996*a*); cell refinement: *SAINT* (Siemens, 1996*b*); data reduction: *SAINT*; program(s) used to solve structures: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structures: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

The authors would like to thank the Malaysian Government and Universiti Sains Malaysia for research grant R&D No. 190-9609-2801. SSSR thanks the Universiti Sains Malaysia for a Visiting Postdoctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1414). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1320–1322

The first mixed iodide–dithiocarbamate complex of selenium(II): *catena*-poly[[(di-*n*-propyldithiocarbamato-*S*,*S*′)selenium(II)]-*μ*-iodo]

S. Rajashree,[a] R. Krishna Kumar,[a] G. Aravamudan,[a] M. R. Udupa,[a] Kandasamy Sivakumar[b]† and Hoong-Kun Fun[b]

[a]*Department of Chemistry, Indian Institute of Technology, Chennai 600 036, India, and* [b]*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia. E-mail: kramanat@unity.ncsu.edu*

(*Received 16 September 1998; accepted 10 March 1999*)

Abstract

The title compound, $[\mathrm{SeI(C_7H_{14}NS_2)}]_n$, was prepared by the oxidative displacement of one of the dithiocarbamates in bis(di-*n*-propyldithiocarbamato)selenium(II) using iodine. This complex has a polymeric structure, with the central Se atoms bridged by the iodine ions. The geometry around each Se atom is planar trapezoidal ($\mathrm{SeS_2I_2}$), with Se—I distances of 3.124 (2) and 3.232 (1) Å. This is the first example of a mixed iodide–dithiocarbamate complex of selenium(II).

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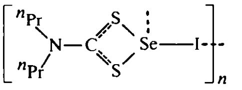
† On leave from the Department of Physics, Anna University, Chennai 600 052, India.

Acta Crystallographica Section C
ISSN 0108-2701 © 1999

Comment

The title compound, (I), was prepared as part of studies on the complexes of selenium in the +II oxidation state and of tellurium in the +II and +IV oxidation states (Rajashree *et al.*, 1996; Krishna Kumar *et al.*, 1993*a*; Krishna Kumar, Aravamudan, Udupa, Seshasayee, Selvam & Yvon, 1996). Iodine reacts with dithiocarbamate complexes of selenium(II) and tellurium(II,IV) in two different ways. It oxidatively adds to tellurium in $\mathrm{Te^{II}}$ complexes (Krishna Kumar, Aravamudan, Udupa, Seshasayee, Selvam & Yvon, 1996); however, with $\mathrm{Te^{IV}}$–dithiocarbamate complexes, it oxidatively displaces the dithiocarbamate (Krishna Kumar *et al.*, 1993*b*). The present studies confirm that in an $\mathrm{Se^{II}}$–dithiocarbamate complex, oxidative displacement occurs, resulting in the formation of iodo(di-*n*-propyldithiocarbamato)selenium(II), which is an interesting result, given that iodide is a good reducing agent for selenium(II) in aqueous solutions.



(I)

The structure determination of the title compound (Fig. 1) shows that it is analogous to Te*LX* (*L* = dithiocarbamate, *X* = I, Br, Cl; Krishna Kumar *et al.*, 1993*a*; Krishna Kumar, Aravamudan, Udupa & Seshasayee, 1996) and $\mathrm{Se(Se_2CNC_4H_8O)I}$ (Bigoli *et al.*, 1983). As a discrete molecular species, selenium in the title complex would have only three coordinating atoms. Since selenium(II) prefers four-coordination, it resorts to supramolecular interactions through the iodide, giving a polymeric structure. These polymers are helical in nature and there are two such chains in the unit cell, running parallel to the [100] direction.

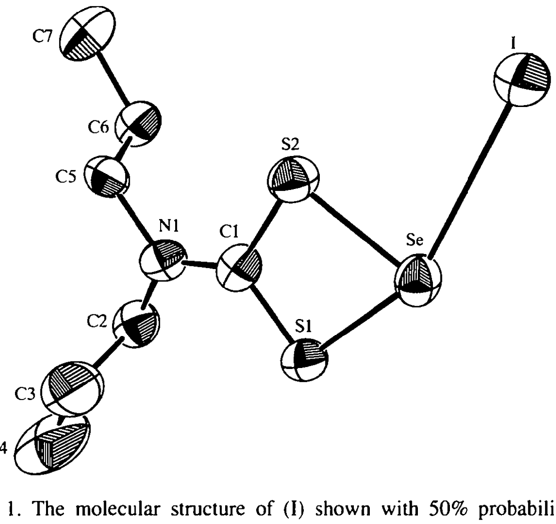


Fig. 1. The molecular structure of (I) shown with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

The asymmetric unit is composed of one iodide and one dithiocarbamate ligand coordinated to selenium. There are two different iodides bound to selenium, one is intramolecular and the other intermolecular; the distances are Se—I = 3.124 (2) and $\mathrm{Se—I^i}$ = 3.232 (1) Å [symmetry code: (i) $\frac{1}{2}+x, \frac{3}{2}-y, 1-z$], which are longer than the sum of the covalent radii of the individual atoms, and the I—Se—I angle is 130.11 (4)°. The dithiocarbamate moiety is coordinated in an isobidentate fashion, the two Se—S distances being 2.298 (3) and 2.277 (3) Å. The angle made by the two S atoms with selenium is 76.84 (11)° and the resulting coordination geometry around selenium is planar trapezoidal. The distance between adjacent Se atoms within a chain is 4.158 (2) Å.

All other geometrical data pertaining to the dithiocarbamate ligand are similar to those observed in numerous previously determined structures. Atoms C3 and C4 are partially disordered, which is an expected phenomenon associated with alkyl groups.

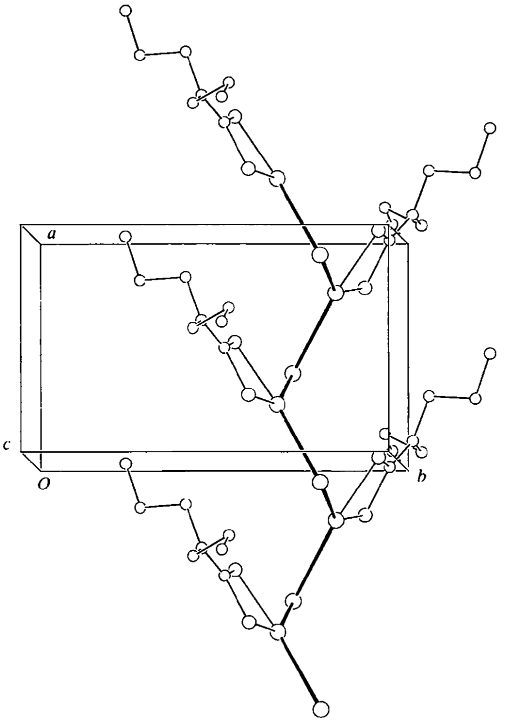


Fig. 2. A packing diagram showing the polymeric chain propagating along [100].

Experimental

A solution (10 ml) of $\mathrm{Se(dnpdtc)_2}$ (0.5 mmol; dnpdtc is di-*n*-propyldithiocarbamate) in $\mathrm{CCl_4}$ was added to iodine (0.5 mmol, 0.125 g) dissolved in $\mathrm{CCl_4}$ (20 ml). The resulting red solution gave a red crystalline product on solvent evaporation at low temperature. The excess iodine and the disulfide formed were removed by repeated washing with CCl_4. The yield of the complex was 0.180 g. Analysis found: C 21.87, H 3.68, N 3.60, Se 20.6, I 32.5%; calculated: C 21.87, H 3.69, N 3.66, Se 20.66, I 33.21%.

Crystal data

[SeI($C_7H_{14}NS_2$)]
$M_r = 382.17$
Orthorhombic
$P2_12_12_1$
$a = 6.905 (3)$ Å
$b = 11.050 (6)$ Å
$c = 16.835 (2)$ Å
$V = 1284.5 (9)$ Å^3
$Z = 4$
$D_x = 1.976$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 36 reflections
$\theta = 8–25°$
$\mu = 5.609$ mm^{-1}
$T = 293 (2)$ K
Needle
0.42 × 0.12 × 0.12 mm
Red–brown

Data collection

Siemens *P*4 diffractometer
θ–2θ scans
Absorption correction: ψ scan (*XSCANS*; Siemens, 1994)
$T_{min} = 0.374$, $T_{max} = 0.510$
1279 measured reflections
1279 independent reflections

1037 reflections with $I > 2\sigma(I)$
$\theta_{max} = 24.97°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 20$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.094$
$S = 1.092$
1279 reflections
109 parameters
H atoms were fixed geometrically and refined using a riding model
$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 1.4891P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.392$ e Å^{-3}
$\Delta\rho_{min} = -0.513$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.00 (4)

Table 1. *Selected geometric parameters (Å, °)*

I—Se	3.124 (2)	Se—I^i	3.232 (1)
Se—S2	2.277 (3)	S1—C1	1.729 (11)
Se—S1	2.298 (3)	S2—C1	1.725 (11)
S2—Se—S1	76.84 (11)	C1—S1—Se	85.8 (4)
S2—Se—I	77.66 (8)	C1—S2—Se	86.5 (4)
S1—Se—I^i	75.23 (8)	S2—C1—S1	110.8 (6)
I—Se—I^i	130.11 (4)		

Symmetry code: (i) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$.

The disorder in atoms C3 and C4 could not be resolved satisfactorily by assigning partial sites.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1008). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1322–1325

(*S*)-8-Chloro-5-methyl-6-(3-methylbut-2-enyl)-2-thioxo-1*H*-4,5,6,7-tetrahydroimidazo[4,5,1-*jk*][1,4]benzodiazepinium bromide methanol solvate†

Oswald M. Peeters, Norbert M. Blaton and Camiel J. De Ranter

Laboratorium voor Analytische Chemie en Medicinale Fysicochemie, Faculteit Farmaceutische Wetenschappen, Katholieke Universiteit Leuven, Van Evenstraat 4, B-3000 Leuven, Belgium. E-mail: maurice. peeters@farm.kuleuven. ac.be

(*Received 29 March 1999; accepted 27 April 1999*)

Abstract

The crystal structure of the title compound, $C_{16}H_{21}ClN_3S^+\cdot Br^-\cdot CH_3OH$, the hydrobromide salt of (*S*)-8-Cl-TIBO (tivirapine), reveals a distorted boat–sofa conformation for the diazepine ring, with the methyl group and the 3-methylbut-2-enyl side chain in equatorial and axial positions, respectively. The protonated N atom has

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† Internal code of the Janssen Research Foundation: R110885.