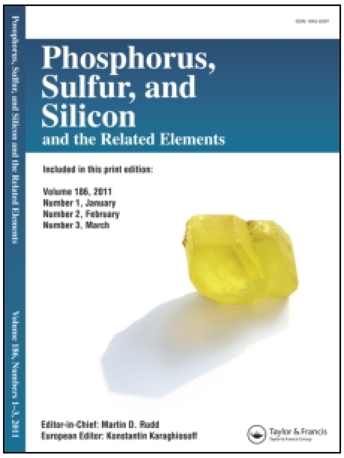

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SYNTHESIS AND STRUCTURE OF THE FIRST MIXED HALIDE-DITHIOCARBAMATE COMPLEX OF SE(II), BROMODIETHYLDITHIO-CARBAMATOSELENIUM(II), [Se{(C$_2$H$_5$)$_2$NCS$_2$}Br]

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SYNTHESIS AND STRUCTURE OF THE FIRST MIXED HALIDE-DITHIOCARBAMATE COMPLEX OF SE(II), BROMODIETHYLDITHIOCARBAMATOSELENIUM(II), [Se{(C_2H_5)$_2$NCS$_2$}Br]

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The title compound, SeLBr [L^- = diethyldithiocarbamate, $(C_2H_5)_2NCS_2^-$] is the first example of Se(II) complex featuring a dithiocarbamate and a halide. It was obtained by the reaction of Se(IV)bromide with tetraethylthiuram disulfide in a methanol solution containing hydrobromic acid. The structure determination of the compound shows it to be polymeric with bromine being the bridging ligand. The crystals of SeLBr are monoclinic with a = 10.391(3), b = 8.434(4), c = 12.030(2) Å, β = 108.10(2)°, V = 1002.15 Å^3, Z = 4 and space group, $P2_1/n$; R = 0.073, R_w = 0.074.

Key words: Se(IV)-thiuram disulfide reaction, bromoselenium(II), dithiocarbamatoselenium(II), bromodiethyldithiocarbamatoselenium(II).

INTRODUCTION

The title compound has been prepared during our continuing studies on the complexes of selenium in +II and tellurium in +II and +IV oxidation states. The interactions of Se(IV) with thiols and dithiolate ligands have been studied extensively. In most of these cases, only Se(II)-thiolate[1-4] or Se(II)-dithiolate[5-10] complexes result. Only when thiourea[11] or substituted thioureas[12-14] are used as ligands, mixed halide-thiourea complexes have been isolated. Despite the knowledge about many selenium(II) dithiocarbamates, (Se[$(R_1R_2)NCS_2]_2$) [$R_1 = R_2 = C_2H_5$,[9] morpholyl,[7] CH_2CH_2OH[10]] there is no report on the isolation of a mixed halide-dithiocarbamate complex of Se(II). On the contrary, numerous studies have been carried out for the preparation of mixed halide-dithiocarbamate complexes of both Te(II) and Te(IV) and the various complexes obtained have been reviewed by Haiduc *et al.*[15] The complexes of the form $Te^{II}LX$(X = I,[16] Br,[17] Cl[17]), Te^{IV} $(dtc)_3X$[dtc = $(C_2H_5)_2NCS_2$; X = I,[18] Cl[19]; dtc = $(HOCH_2CH_2)_2NCS_2$; X = I,[10] Cl[20]; dtc = $(CH_3)(HOCH_2CH_2)$-NCS_2, X = Br,[21,22] Cl[21,23]] and $Te^{IV}(dtc)_2X_2$ [dtc = $(C_2H_5)_2NCS_2$, X = I,[24] Br[25]; dtc = $(HOCH_2CH_2)_2NCS_2$, X = I[20,26]] have been prepared and their crystal structures determined. Using suitable synthetic methods we have now been able to prepare the novel compound, bromodiethyldithiocarbamatoselenium(II), SeLBr. In this paper, the preparation and the crystal structural study of this compound is reported.

EXPERIMENTAL

Preparation of SeLBr

To 50 ml methanol solution containing 2.0 mmol (0.593 g) of tetraethylthiuram disulfide (L—L), 2.0 mmol (0.220 g) of SeO_2 dissolved in 2 ml 9M HBr was added at 0°C and the contents were stirred for about 10 minutes. An orange red solid separated out, was filtered, washed with carbon tetrachloride and air dried. Yield was 0.553 g (90%). Recrystallization from a dichloromethane-carbon tetrachloride mixture (1:1 v/v) yielded red crystals. The composition of the compound was found to correspond to $SeC_5H_{10}NS_2Br$. Elemental analysis (wt %). Found: C, 19.53; H, 3.20; N, 4.50; S, 20.80; Br, 25.5; and Se, 25.58. Calculated: C, 19.55; H, 3.28; N, 4.55; S, 20.88; Br, 26.01 and Se, 25.71. By using tetra-*n*-propylthiuram disulfide, instead of tetraethylthiuram disulfide in the above reaction, the equally stable bromodi-*n*-propyldithiocarbamatoselenium(II) was isolated in 90–95% yield.

At room temperature, the filtrate after separation of SeLBr, yielded a small quantity of yellow fibrous material over a period of 3 hours. It was insoluble in methanol and water, very sparingly soluble in dichloromethane and benzene and highly soluble in carbon disulfide. The elemental composition was found to correspond to Se_2S_6. (Wt%) Found: Se, 42.87 and S, 54.22. Calculated: Se, 45.08 and S, 54.92. It is found to be one of the Se—S 'alloys' about which extensive work has been reported.[27]

Products other than SeLBr and Se_2S_6 are also formed in the above reaction. Hence to understand the exact stoichiometry of the reaction, experiments with various mole ratios of Se(IV) oxide and L—L, keeping other conditions the same, have been worked out.

Crystal Data

A single crystal of SeLBr of dimension 0.1 × 0.3 × 0.4 mm^3 was mounted on an Enraf-Nonius CAD4 diffractometer fitted with MoK_α radiation. The unit cell parameters were determined from 25 reflections in the θ range 8 to 15°. In Table I the crystal data and data collection parameters are listed. The intensity data were collected by the $\omega - 2\theta$ scan technique to a maximum 2θ value of 50°. 2048 reflections were measured of which only 1328 reflections were unique. Two standard reflections were remeasured every hour. They showed no significant intensity variation (<5.0%). The data were corrected for Lorentz and polarization effects. Absorption correction was applied using SHELX 76.[28]

The structure was solved by the heavy atom method. The positions of Se and Br were obtained from the Patterson map, and based on their positions, the difference Fourier map gave the positions of all other non-hydrogen atoms. The refinement was carried out by the full matrix least squares method using SHELX 76. The non-hydrogen atoms were refined anisotropically and the position of the hydrogen atoms were located. Ninety-one parameters were refined using 823 reflections with $I > 3\sigma(I)$ and the refinement was terminated when the maximum shift per e.s.d. was 0.03. The R factor at this stage was 0.073 and $R_w = 0.074$. The final difference Fourier map showed a maximum electron density of 1.41 $e\text{Å}^{-3}$ which was found to be close to the heavy atom, selenium and does not have any chemical significance. Atomic scattering factors for non-hydrogen atoms were taken from Cromer and Mann[29] and anomalous dispersion correction factors were taken from Cromer and Liberman.[30] ‡

RESULTS AND DISCUSSION

Structure of SeLBr

Selenium(II) complexes are either two, three or four coordinated depending on the nature of the ligands. The two coordinated complexes have a bent structure[4] and the four coordinated have planar trapezoidal[7,9,10] or square planar geometry[11] as observed from numerous previous structure determinations. The selenium(II)-dithiocarbamates[7,9,10] generally have four coordination and the SeS_4 moiety has a planar trapezoidal geometry. In the title compound, if it were to exist as a monomer, selenium would be coordinately unsaturated, being bound to two sulfur atoms of the dithiocarbamate and a bromine atom.

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‡The anisotropic thermal parameters for non-hydrogen atoms have been deposited with the Cambridge Crystallographic Date Centre (CCDC), UK.

TABLE I

Crystal data for $Se[(C_2H_5)_2NCS_2]Br$

Formula	$Se C_5H_{10}NS_2Br$
Molecular weight	307.13
Crystal system, space group	Monoclinic, $P2_1 / n$
a(Å)	10.391(3)
b(Å)	8.434(4)
C(Å)	12.030(2)
β (°)	108.10(2)
Volume (Å^3)	1002.15
Z	4
Density (measured) Mgm^{-3}	2.04
Density (Calculated) Mgm^{-3}	2.04
Absorption coefficient μ(mm^{-1})	7.88
Data collection instrument	Enraf Nonius CAD-4
Radiation used, (wavelength)	MoK$_\alpha$ (0.71069)
Scan method	$\omega - 2\theta$
No. of reflections measured	2048
No. of reflections with $I > 3\sigma(I)$	823
No. of reflections for lattice parameters	25
Transmission factors : max, min	0.510, 0.126
R_{int}	0.009
R	0.073
R_w, $w = 4.659 / [\sigma^2 \mid F \mid + 0.000947 \mid F \mid^2$	0.074

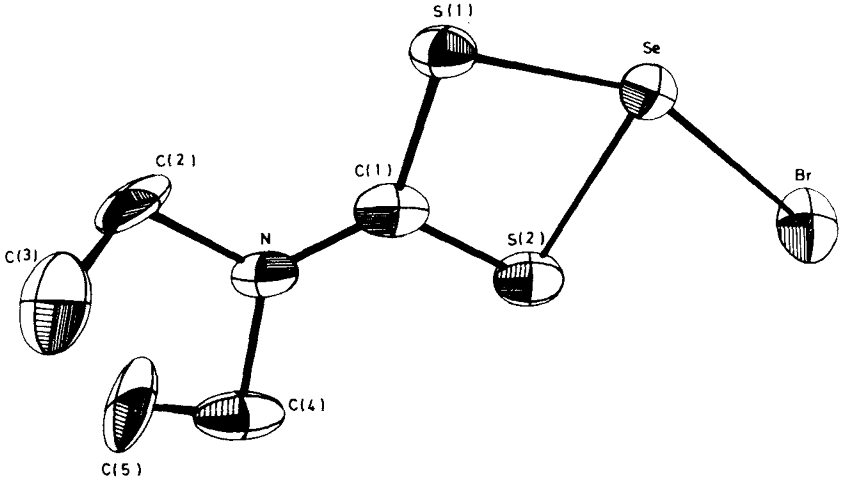

FIGURE 1 The ORTEP diagram of a molecule of SeLBr with 50% probability ellipsoids.

TABLE II

Fractional atomic coordinates (Å^2) of all non-hydrogen atoms with e.s.d's in parentheses

Atom	x/a	y/b	z/c	U_{eq}
Se	0.8598(3)	0.0145(3)	0.8063(2)	0.056(1)
Br	0.6115(3)	0.1858(3)	0.7821(3)	0.088(2)
S(1)	0.0905(7)	-0.0106(7)	0.8497(5)	0.060(3)
S(2)	-0.0635(8)	0.2535(7)	0.8814(5)	0.064(4)
C(1)	0.098(3)	0.183(3)	0.894(2)	0.060(1)
N	0.206(2)	0.268(2)	0.934(2)	0.060(1)
C(2)	0.341(3)	0.205(3)	0.937(2)	0.080(2)
C(3)	0.436(3)	0.199(3)	1.064(2)	0.090(2)
C(4)	0.197(3)	0.434(3)	0.974(2)	0.080(2)
C(5)	0.251(3)	0.551(4)	0.904(3)	0.100(2)

There are three distinct possibilities by which four coordination could be attained. In the first case, selenium can bind to another selenium atom to form a dimer having a Se—Se bond. The dithiocarbamate group can act as a bridging ligand, as observed in $(MoL_3)_2$,[31] $(ZnL_2)_2$[32] and $(Ru_2L_5)BF_4$[33] and in the second case similar dithiocarbamate bridged complexes can get formed. The third possibility is the coordination of the bromide of the neighbouring group to selenium to form bromide bridged

TABLE III

Selected bond lengths (Å) and bond angles (°)

Se - Br	2.892(4)	C(1) - N	1.29(3)
Se - Br	3.016(4)	N - C(2)	1.48(3)
Se - S(1)	2.299(7)	N - C(4)	1.50(3)
Se - S(2)	2.251(6)	C(2) - C(3)	1.55(4)
S(1) - C(1)	1.71(2)	C(4) - C(5)	1.51(4)
S(2) - C(1)	1.74(3)		
Br - Se - Br	127.3(3)	S(1) - C(1) - S(2)	110(2)
Br - Se - S(1)	154.6(3)	S(1) - C(1) - N	127(2)
Br - Se - S(2)	77.7(3)	S(2) - C(1) - N	123(2)
Br - Se - S(1)	77.6(3)	C(1) - N - C(2)	121(2)
Br - Se - S(2)	154.5(4)	C(1) - N - C(4)	120(2)
S(1) - Se - S(2)	77.1(3)	N - C(2) - C(3)	110(2)
C(1) - S(1) - Se	86(1)	N - C(4) - C(5)	111(2)
C(1) - S(2) - Se	86.7(8)	C(4) - N - C(2)	119(2)

(') = 0.5 - x, 0.5 + y, 0.5 - z

dimeric or polymeric structure. Such halide bridged complexes, have been reported in the tellurium(IV) complexes, TeL_2I_2,[24] $Te[(HOCH_2CH_2)_2NCS_2]_2I_2$[26] and $Te_2L_3I_3$[34] and for the tellurium(II) complexes, TeLX (X = I,[16] Br,[17] Cl[17]) and $Te[(S_2COC_2H_5)Br]_n$.[35]

The ORTEP[36] diagram of a molecule of SeLBr is shown in Figure 1. The final fractional atomic coordinates of all non-hydrogen atoms are given in Table II and the bond lengths and bond angles in Table III. The crystal structure of SeLBr is very similar to that of (N-morpholinecarbodiselenoato)selenium(II)iodide[37] and that of the recently reported iododiethyldithiocarbamatotelurium(II).[16] As found in the tellurium analogue the selenium atom is bound to two sulfur atoms S(1) and S(2) at distances of 2.299(7) and 2.251(6) Å, which are shorter than the average Se—S distance of 2.54 Å found in SeL_2. This may be attributed to the binding of a single dithiocarbamate, which is a stronger complexing ligand than bromide, to Se(II) in SeLBr compared to the two dithiocarbamates bound to Se(II) in SeL_2. Also, the dithiocarbamate is bound in a much more symmetrical manner, as the difference between the two Se—S distances is small. The intra ligand S(1)-Se—S(2) angle is 77.1(3)°. The bromine atom, Br, is bound to selenium at a distance of 2.892(4) Å and another bromine atom Br′ of the neighbouring SeLBr moiety has an intermolecular interaction at 3.016(4) Å. The two Se—Br distances are longer than the sum of the covalent radii of selenium and bromine atoms (2.31 Å),[38] which can be attributed to

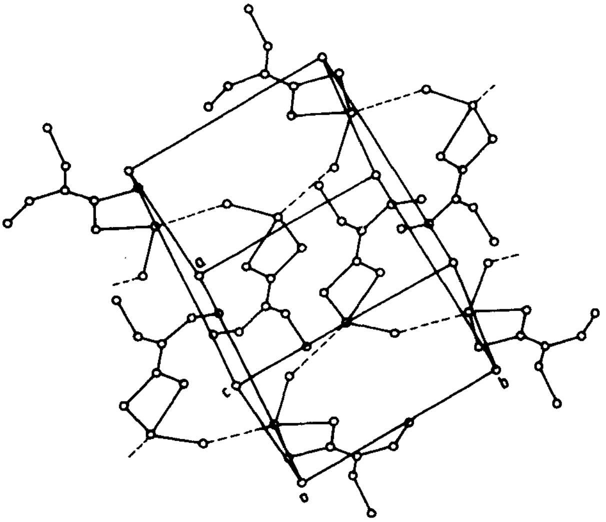

FIGURE 2 Packing diagram of the molecules in a unit cell showing the polymeric chain propagation along the *c* axis.

two reasons. The first being the *trans* influence of the sulfur atom of the dithiocarbamate and secondly, the bridging nature of the bromine atoms. The Br—Se—Br′ angle is 127.3(3)° and S(1)-Se—Br angle is 77.6(3)°. With these four ligand atoms selenium has a planar trapezoidal geometry. The R.M.S. deviation of the five atoms from the mean plane is 0.035 Å.

In the dithiocarbamate ligand, all geometric parameters conform to the previously observed values in other complexes containing this ligand. In the characteristic C═N IR absorption region for dithiocarbamates, SeLBr showed absorption at 1523 cm^{-1} and SeL_2 at 1490 cm^{-1}. The shift to higher wave numbers in SeLBr is due to stronger binding of the dithiocarbamate than in SeL_2.

The bromine bridged polymeric SeLBr molecules have a helical configuration. Two pairs of selenium and bromine atoms form the period of the helix, which is 8.432(4) Å. Two such polymeric chains run parallel to each other along the *c* axis in a unit cell as shown in Figure 2. The shortest separation between the two helices is 4.677(5) Å, which is the interchain Se—Se distance. Within each helix the two neighbouring selenium atoms are separated by 4.786(4) Å and the bromine atoms by 5.294(5) Å.

It is of interest to point out that the molecular weight determination in benzene solution showed the molecules to be monomeric in solution.

Stability of SeLBr and SeLCl

SeLBr is indefinitely stable as a solid and also when dissolved in dichloromethane or benzene. Its solutions in methanol containing 2M HBr are also stable. However, SeLBr solutions in methanol in absence of HBr are unstable. In order to establish the products formed and the mechanism by which the decomposition proceeds, (0.204 g) 0.66 mmol of SeLBr in 50 ml of methanol was refluxed for 3 hours and the volatile matter bubbled through an aqueous solution of Ni(II) acetate and di(2-hydroxyethyl)amine mixture. A green solid of bis(2,2′-dihydroxyethyldithiocarbamato)nickel(II)[39] formed confirms the evolution of carbon disulphide. The non-volatile matter in the reaction mixture which was filtered to separate the reduced elemental selenium and the filtrate, on evaporation yielded diethylammonium bromide.

Attempts were made to prepare SeLCl via two approaches: (1) by the interaction of Se(IV) with L—L in conc. HCl media and (2) by the interaction of SeLBr dissolved in dichloromethane with suspension of AgCl. By both the methods, an oily liquid analysing as SeLCl was found to be formed. However, rapid decomposition to Se and other products occurred during attempts to crystallize the SeLCl, indicating that coordination of chloride to Se(II) is not strong enough to ensure stability to the SeLCl species.

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