Reactions between Selenocyanate and Bromine. Syntheses and Crystal Structures of Phenyltrimethylammonium Salts of Dibromoselenocyanate, $[C_6H_5(CH_3)_3N][SeCNBr_2]$, and Bromodiselenocyanate, $[C_6H_5(CH_3)_3N][(SeCN)_2Br]$

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In reactions between selenocyanate and bromine, the composition of the product depends on the solvent used. The compounds $[C_6H_5(CH_3)_3N][SeCNBr_2]$ (**1**) and $[C_6H_5(CH_3)_3N][(SeCN)_2Br]$ (**2**) were prepared in dichloromethane. Compound **1** forms monoclinic crystals, space group $P2_1/c$ with $Z = 4$, and $a = 6.166(1)$, $b = 9.381(1)$, $c = 23.892(2)$ Å and $\beta = 96.03(1)°$. Compound **2** forms orthorhombic crystals, space group $P2_1nb$ with $a = 6.795(1)$, $b = 10.212(1)$ and $c = 21.521(2)$ Å. The structures were determined by X-ray methods and refined to $R = 0.060$ (**1**) and 0.054 (**2**) for 1303 and 1293 observed reflections, respectively. In compound **1** the selenium atom has a T-shaped coordination with a nearly linear Br–Se–Br sequence, and Se–Br distances of 2.624(2) and 2.530(2) Å. *Trans* to the Se–C bond there is a close contact to a selenocyanate N atom of an adjacent anion with a distance of 3.195(9) Å and a C–Se···N angle of 173.9(4)°. In compound **2** the Se–Se–Br sequence is nearly linear with Se–Se = 2.404(2) Å and Se–Br = 3.036(2) Å. The C–Se–Se–C torsion angle is −79.4(5)°. *Trans* to the Se–C bonds there are close contacts to Br atoms with a distance of 3.530(2) Å for the terminal and 3.290(2) Å for the central selenocyanate group, and C–Se···Br angles of 163.2(5) and 178.0(4)°, respectively. *Trans* to the Se–Se bond there is close contact to a N atom of an adjacent anion with a distance of 3.160(15) Å and Se–Se···N angle of 165.3(3)°.

Triselenocyanate, $(SeCN)_3^-$, selenium triselenocyanate, $Se(SeCN)_3^-$, and selenium diselenocyanate, $Se(SeCN)_2$, have been reported as products in the reaction between aqueous selenocyanate and bromine dissolved in benzene.[1] Dibromoselenocyanate, $SeCNBr_2^-$, and bromodiselenocyanate, $(SeCN)_2Br^-$, have been isolated as phenyltrimethylammonium salts from the same reactants by the use of dichloromethane as solvent. The reactions and the crystal structures of the salts are discussed here.

Experimental

Preparations. $PhMe_3NSeCN$ was prepared by dissolving 0.2 mol (28.8 g) KSeCN in 70 ml CH_3OH at room temperature, adding 0.2 mol (43.2 g) $PhMe_3NBr$ and stirring the suspension for 20 min. Heating was avoided to prevent decomposition. The mixture was filtered and the precipitated KBr washed with CH_3OH. Dried ether (300 ml) was added to the combined solutions, and immediately precipitation of colourless crystals took place. The crystals were washed with ether. Yield 47.7 g (99 %).

$[PhMe_3N][SeCNBr_2]$. To a suspension of 1 mmol (0.241 g) $PhMe_3NSeCN$ in 1 ml CH_2Cl_2 was added 1 mmol (0.160 g) Br_2 as a 10 % solution in CH_2Cl_2. After refrigeration for 0.5 h, small yellow flakes were deposited. 7.5 ml CH_2Cl_2 and 0.5 ml ether were then added. The solution was gently heated, filtrated and set aside at room temperature, then in a refrigerator and finally in a freezer. 0.30 g yellow–orange crystals separated, which is 75 % of the theoretical value based on eqn. (6) (see later).

$[PhMe_3N][(SeCN)_2Br]$. To 2 mmol (0.483 g) $PhMe_3NSeCN$ in 3 ml CH_2Cl_2 was added 1 mmol (0.160 g) Br_2 as a 10 % solution in CH_2Cl_2. The resulting solution was set aside in the cold. Yield: 0.36 g of long yellow prisms, which is 85 % of theoretical value based on eqn. (5) (see later).

X-Ray structure analyses. The determination of unit cell parameters and the data collections were carried out on an ENRAF–NONIUS CAD4 diffractometer, using monochromated MoK_α radiation ($\lambda = 0.71069$ Å). Crystal data and conditions for data collections are given in Table 1. The cell parameters were based on a least-squares fit of accurate setting angles for 24 reflections. Intensities were corrected for Lorentz and polarization effects, decay and absorption. The crystal shape of **2** was not well defined, and

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Table 1. Crystallographic data.

	Compound **1**	Compound **2**
Compound	$PhMe_3NSeCNBr_2$	$PhMe_3N(SeCN)_2Br$
Formula	$C_{10}H_{14}Br_2N_2Se$	$C_{11}H_{14}N_3Se_2$
M	401.0	426.1
System	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1nb$
a/Å	6.166(1)	6.795(1)
b/Å	9.381(1)	10.212(1)
c/Å	23.892(2)	21.521(2)
β/°	96.03(1)	
V/Å^3	1374.4(5)	1493.5(4)
Z	4	4
T/K	293	293
D_{calc}/g cm^{-3}	1.938	1.895
F(000)	768	816
Θ_{max}/°	30	30
Scan mode	ω	ω
Scan speed/° min^{-1}	2.75	2.75
Min. scan width/°	1.30	1.30
Loss of intensity (%)	23.4	1.8
μ(MoK_α)/cm^{-1}	84.4	75.4
Crystal volume/mm^3	0.0015	0.0020
Correction for absorption	Numerical	Empirical[a]
Transmission factors	0.205–0.803	
Correction factors		0.73–1.08
No. of independent measurements	3988	2338
No. with $I > 2\sigma(I)$	1303	1293
No. of parameters refined	136	153
$R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.060	0.054
$R_w = [\Sigma w(F_o-F_c)^2/\Sigma wF_o^2]^{1/2}$	0.053	0.047
$S = [\Sigma w(F_o-F_c)^2/(n-m)]^{1/2}$	1.195	1.091
Max. Δ(ϱ)/e Å^{-3}	0.79	0.98

[a] Ref. 2.

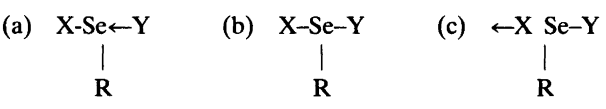
therefore the empirical method of the program package was used for absorption corrections. Reflections with $I > 2\sigma(I)$ were regarded as observed. The sample used for compound **1** was a thin plate and for **2** it was a thin needle, and there were relatively many weak reflections.

The structures were solved by direct (MULTAN) and Fourier difference methods and refined by least-squares calculations, using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed geometrically with bond lengths N–H = 0.87 and C–H = 0.95 Å, and were held fixed, with isotropic thermal parameters equal to $1.3B_{eq}$ for the atoms to which they are attached. Secondary extinction effects were found to be negligible. Since **2** belongs to an acentric space group, the structure was also refined with inverted coordinates whereby the *R*- and *S*-values increased slightly. The programs used were the Enraf–Nonius Structure Determination Package, 1987.

Atomic coordinates of non-hydrogen atoms are given in Table 2. Hydrogen coordinates, thermal parameters, and complete lists of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

Results and discussion

The present types of complexes have been looked upon as intermediates in the nucleophilic displacement reaction on a divalent chalcogen.[3,4] The displacements take place through the approach of a nucleophile *trans* to the leaving group. The bonds in the complexes are based on p-orbitals of the central chalcogen atom, the bond angles being close to 90 and 180°. Two types of bonds occur. One is the ordinary two-centre, two-electron (2c–2e) bond formed by the overlap of a p-orbital of the central chalcogen atom with a σ-orbital of the ligand. The other is the linear three-centre, four-electron (3c–4e) bond formed from a p-orbital of the central chalcogen atom and one σ-orbital from each of the two ligands. The latter type has only two bonding electrons for two bonds. These bonds are longer and weaker than a 2c–2e bond.[5] With divalent selenium as the central atom, the nucleophilic displacement can be visualized through the following three stages:



The bond angle in molecules of divalent selenium[6] is about 103°, and the bond lengths are as expected for single covalent bonds, the sum of the covalent radii. When the nucleophilic attack starts (a) the bond length in the *trans* position

Table 2. Fractional atomic coordinates with e.s.d.s in parentheses.

Atom	*x*	*y*	*z*	B_{eq}/Å^2
(a) $[C_6H_5(CH_3)_3N][(SeCN)Br_2]$ (**1**)				
Se	0.54633(19)	0.25428(13)	0.34632(5)	3.16(2)
Br(1)	0.50415(21)	0.07183(14)	0.26263(5)	4.22(3)
Br(2)	0.55817(22)	0.42565(14)	0.42833(6)	5.03(3)
C(1)	0.2438(18)	0.2440(12)	0.3450(5)	3.4(2)
N(1)	0.0631(14)	0.2374(11)	0.3456(4)	4.4(2)
N(2)	0.9186(13)	0.2549(9)	0.1455(4)	2.9(2)
C(21)	0.9993(21)	0.3342(14)	0.1974(5)	4.9(3)
C(22)	0.9568(21)	0.0984(13)	0.1591(5)	4.8(3)
C(23)	0.6757(18)	0.2805(14)	0.1337(6)	4.7(3)
C(24)	1.0255(17)	0.2955(10)	0.0943(5)	2.9(2)
C(25)	1.1607(17)	0.4104(11)	0.0958(4)	3.2(2)
C(26)	1.2535(19)	0.4458(13)	0.0477(6)	4.9(3)
C(27)	1.2154(19)	0.3651(15)	−0.0007(5)	4.8(3)
C(28)	1.0794(21)	0.2489(14)	−0.0019(6)	5.5(3)
C(29)	0.9835(20)	0.2151(11)	0.0467(5)	4.1(3)
(b) $[C_6H_5(CH_3)_3N][(SeCN)_2Br]$ (**2**)				
Se(1)	0.31530(26)	0.72499(12)	0.04032(5)	3.21(2)
Se(2)	0.62283(23)	0.83974(11)	0.04937(5)	2.85(2)
Br	1.0	0.99009(13)	0.07447(6)	3.54(2)
C(1)	0.4227(19)	0.5758(12)	0.0059(6)	3.7(3)
C(2)	0.6915(20)	0.7478(13)	0.1217(5)	3.8(3)
N(1)	0.4811(19)	0.4832(13)	−0.0418(13)	5.4(3)
N(2)	0.7297(18)	0.6906(13)	0.1653(11)	5.6(3)
N(3)	1.0223(15)	0.7740(9)	0.8477(9)	2.9(2)
C(31)	1.0613(22)	0.9027(15)	0.8161(6)	5.4(4)
C(32)	1.2104(24)	0.6965(18)	0.8476(8)	7.2(5)
C(33)	0.9736(22)	0.8101(13)	0.9131(5)	4.3(3)
C(34)	0.8666(17)	0.6964(10)	0.8163(5)	2.9(3)
C(35)	0.7774(24)	0.5961(13)	0.8485(6)	4.8(4)
C(36)	0.6386(25)	0.5214(13)	0.8204(7)	5.1(3)
C(37)	0.5863(20)	0.5458(13)	0.7595(7)	4.7(3)
C(38)	0.6705(21)	0.6457(14)	0.7288(6)	4.7(3)
C(39)	0.8158(23)	0.7215(13)	0.7567(5)	3.9(3)

increases and the bond angle decreases. In the intermediate (b) and with two bonds of equal strength, the bond lengths are longer than single covalent bonds and the bond angles are 90 and 180°. In the last stage, where the leaving group departs, the new bond angle increases, and the bond length decreases to a normal covalent bond length.

Structures. The selenium anion complexes of the present study are depicted in Fig. 1, together with the most essential bond lengths. Full details of bond lengths and angles are given in Table 3.

In the $SeCNBr_2^-$ ion the Br–Se–Br sequence is nearly linear. The angle is 175.73(7)°, and the bending, probably due to lone-pair repulsion, is towards the selenocyanate carbon. The two Se–Br bond lengths, 2.624(2) and 2.530(2) Å, are related to the Br–Se–C angles 86.2(3) and 89.6(3)°, respectively. As expected, the repulsion has the greatest influence on the longest bond, which is thus related to the smallest bond angle. The closest interionic contacts to the Br atoms occur for a Se atom at a distance of 3.947(2) Å from Br(1) with the Se···Br(1)–Se angle 171.70(5)°, and

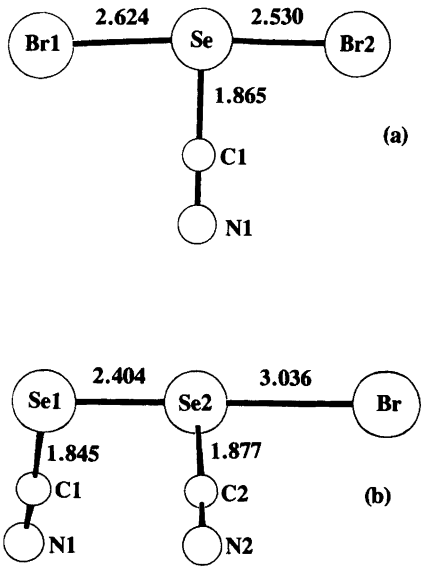


Fig. 1. Views of the $(SeCN)Br_2^-$ ion (a) and the $(SeCN)_2Br^-$ ion (b) as found in the phenyltrimethylammonium salts.

for a Br atom at a distance of 3.835(3) Å from Br(2) with the Se–Br(2)···Br angle 158.44(8)°. However, these interactions are rather weak,[7] and hardly explain the asymmetry of the Br–Se bond lengths in the Br(1)–Se–Br(2) sequence. In the crystal structure of the corresponding tetramethylammonium salt[6] Se lies in a mirror plane, and the two Se–Br bonds are thus equal. Furthermore, the Se–Br bond lengths and the Br–Se–C bond angles therein are, within experimental error, equal to the mean values of corresponding bonds and angles in the present structure.

In $(SeCN)_2Br^-$ the Se–Se–Br angle is 174.17(6)°, and the bending here is also towards the central selenocyanate carbon. The Se–Se bond length, 2.404(2) Å, is only 0.09 Å longer than a single covalent bond, whereas the Se–Br bond, 3.036 Å, is 0.73 Å longer than the sum of the covalent radii.[7] The Se–Br bond in this ion is 0.46 Å longer than the average of the corresponding bonds in $SeCNBr_2^-$. The terminal Se–Se–C bond angle is 95.2(5)° and the central Se–Se–C bond angle is 92.3(5)°. The C–Se–Se–C torsion angle is −79.4(5)°.

Table 3. Distances (in Å) and angles (in °) with e.s.d.s in parentheses.

(a) $[(SeCN)Br_2]^-$ (**1**)			
Se–Br(1)	2.624(2)	Br(1)–Se–Br(2)	175.73(7)
Se–Br(2)	2.530(2)	Br(1)–Se–C(1)	86.24(34)
Se–C(1)	1.865(12)	Br(2)–Se–C(1)	89.63(34)
C(1)–N(1)	1.115(12)	Se–C(1)–N(1)	179.5(1.3)
(b) $[(SeCN)_2Br]^-$ (**2**)			
Se(1)–Se(2)	2.404(2)	Se(1)–Se(2)–Br	174.17(6)
Se(2)–Br	3.036(2)	Se(2)–Se(1)–C(1)	95.23(46)
Se(1)–C(1)	1.845(13)	Se(1)–Se(2)–C(2)	92.26(45)
Se(2)–C(2)	1.877(13)	Br–Se(2)–C(2)	84.01(45)
C(1)–N(1)	1.118(16)	Se(1)–C(1)–N(1)	177.4(1.4)
C(2)–N(2)	1.135(15)	Se(2)–C(2)–N(2)	178.6(1.5)

Trans to the Se–C bond in $SeCNBr_2^-$ there is a close contact from the selenium atom to a selenocyanate N atom in an adjacent anion, at a distance of 3.195(9) Å and with the C–Se···N angle 173.9(4)°. In $(SeCN)_2Br^-$ both Se atoms form close contacts to Br atoms; *trans* to the central Se–C bond with a distance of 3.290(2) Å and C–Se···Br angle 178.0(4)°, and *trans* to the terminal Se–C bond with a distance of 3.530(2) Å and C–Se···Br angle 163.5(5)°. *Trans* to the Se–Se bond there is a selenocyanate N atom with a distance of 3.161(14) Å and Se–Se···N angle 165.3(3)°. By taking these contacts into account, the selenium atom has approximately planar four-coordination in both structures.

The Se–C bonds are within error equal to the single $Se–C_{sp}$ bond length, 1.857 Å; the sum of the single-bond radii of selenium, 1.17 Å,[7] and sp-hybridized carbon, 0.687 Å.[8] Within error all the Se–C–N bond angles are 180°.

The dimensions of the phenyltrimethylammonium ion are found to be N–C = 1.484(14)–1.517(14) Å, C–C = 1.344(20)–1.394(17) Å, C–N–C = 104.5(1.0)–114.7(8)°, C–C–C = 118.4(1.2)–121.2(1.1)°.

Oxidation of selenocyanate with bromine to divalent selenium compounds. From the standard reduction potential of the selenocyanogene/selenocyanate couple, 0.57 V,[9] and that of the bromine/bromide couple, 1.07 V,[10] reaction (1)

$$2\ SeCN^- + Br_2 = (SeCN)_2 + 2\ Br^- \quad (1)$$

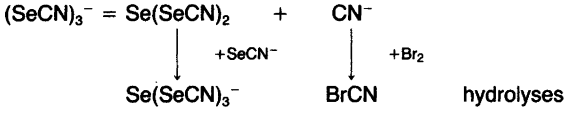
should go far to the right. It has previously been found[1] that bromine, dissolved in benzene, acting on concentrated aqueous solutions of the selenocyanate ion gives three different products, depending on the amount of bromine used [reactions (2)–(4)]. The $(SeCN)_3^-$ and $Se(SeCN)_3^-$ ions were isolated from the aqueous phase as alkali or

$$3\ SeCN^- + Br_2 = (SeCN)_3^- + 2\ Br^- \quad (2)$$

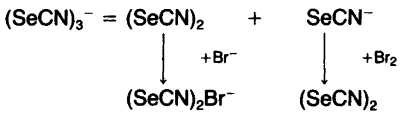
$$4\ SeCN^- + 2\ Br_2 = Se(SeCN)_3^- + BrCN + 3\ Br^- \quad (3)$$

$$3\ SeCN^- + 2\ Br_2 = Se(SeCN)_2 + BrCN + 3\ Br^- \quad (4)$$

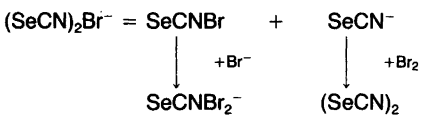
tetramethylammonium salts, whereas seleniumdiselenocyanate was isolated from the benzene phase.



Scheme 1. Reactions in water/benzene.



Scheme 2. Reactions in dichloromethane.



Scheme 3.

In the present work, phenyltrimethylammonium selenocyanate was reacted with bromine dissolved in dichloromethane, reactions (5) and (6), and two new products were

$$2\ SeCN^- + Br_2 = (SeCN)_2Br^- + Br^- \quad (5)$$

$$SeCN^- + Br_2 = SeCNBr_2^- \quad (6)$$

isolated as phenyltrimethylammonium salts. The relative amounts of selenocyanate and bromine are the same in reactions (3) and (5), the difference being the solvents. The reactions can be explained by Schemes 1 and 2, starting with the triselenocyanate ion of reaction (2). In both schemes the ligands leaving the complex are known to be better nucleophiles than the incoming groups. The results of the reactions will therefore depend on the solubility of the complex formed and on the efficiency of the removal of the dissociated ligands from the solutions.

The ligand exchange of Scheme 2 can, by addition of more bromine, give $SeCNBr_2^-$ via reaction (6) [Scheme (3)].

That selenocyanate is a better nucleophile towards divalent selenium than bromide is also visualized by the crystal structure of the $(SeCN)_3^-$,[11] $SeCNBr_2^-$ and $(SeCN)_2Br^-$ ions. In $(SeCN)_3^-$ the two Se–Se bonds are 2.650(3) Å, in $SeCNBr_2^-$ the two Se–Br bonds are 2.624(2) and 2.530(2) Å, and in $(SeCN)_2Br^-$ the Se–Se bond is 2.404(2) Å and the Se–Br bond is 3.041(2) Å. This shows that the Se–Br bond is drastically weakened by a SeCN group in the *trans* position, and it must be concluded that it is easier for a Br^- ion to leave the central selenium atom than it is for the $SeCN^-$ ion to do so.

References

1. Hauge, S. *Acta Chem. Scand. 25* (1971) 3081.
2. Walker, N. and Stuart, D. *Acta Crystallogr., Sect. A 39* (1983) 158.
3. Foss, O. *Pure Appl. Chem. 24* (1970) 31.
4. Foss, O. *Acta Chem. Scand. 16* (1962) 779.
5. Cotton, F. A. and Wilkinson, G. *Advanced Inorganic Chemistry,* 5th edn., John Wiley, New York, N.Y. 1988, p. 188.
6. Bjørnevåg, S., Gahre, P. U., Hauge, S. and Vikane, O. *Acta Chem. Scand., Ser. A 38* (1984) 175.
7. Pauling, L. *The Chemical Bond,* Cornell University Press, Ithaca, NY 1967.
8. Bastiansen, O. and Tretteberg, M. *Tetrahedron 17* (1962) 147.
9. Austad, T. *Acta Chem. Scand., Ser. A 29* (1975) 895.
10. Latimer, W. M. *Oxidation Potentials,* 2nd edn., Prentice-Hall, Englewood Cliffs, NJ 1952, p. 62.
11. Hauge, S. *Acta Chem. Scand., Ser. A 29* (1975) 163.

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