

The Crystal Structure of Bis(phenyltrimethylammonium) Di- μ -bromobis-[di- μ -bromobis{dibromoselenate(II)}], $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2\text{Se}_4\text{Br}_{14}$

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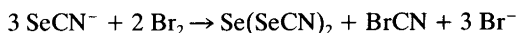
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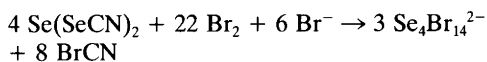
The compound $[\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}]_2\text{Se}_4\text{Br}_{14}$ forms triclinic crystals, space group $P\bar{1}$ (No. 2) with $Z = 1$, and $a = 9.247(2)$, $b = 11.162(1)$, $c = 11.680(1)$ Å, $\alpha = 64.54(1)$, $\beta = 70.13(1)$ and $\gamma = 89.71(1)^\circ$. The structure has been determined by X-ray methods and refined to $R = 0.069$ for 2114 observed reflections. The anion consists of two dinuclear, di-Br-bridged, planar Se_2Br_6 groups, linked together through two linear Se-Br-Se bridges perpendicular to the Se_2Br_6 coordination planes. The bond lengths for the linear bridge are 2.606(2) and 2.608(2) Å. The bridging bond lengths in the Se_2Br_6 group are 2.763(2)–2.790(2) and the terminal bond lengths 2.407(2)–2.416(2) Å. The total lengths of the linear three-centre systems are 5.179(2)–5.214(2) Å.

Dedicated to Professor Olav Foss on his 70th birthday

Oxidation products of the selenocyanate ion have been known for a long time.¹ With bromine, the selenocyanate ion reacts to give selenium diselenocyanate, cyanogen bromide and bromide:²



By use of more bromine, the oxidation can go further. The formation of the ion $\text{Se}_4\text{Br}_{14}^{2-}$ can be summarized as follows:



The $\text{Se}_4\text{Br}_{14}^{2-}$ ion has been isolated as the phenyltrimethylammonium salt, and the crystal structure of the salt is reported here.

Experimental

Preparation. A solution of $\text{C}_6\text{H}_5(\text{CH}_3)_3\text{NBr}$ (0.60 g) and Br_2 (1.00 g) in CH_3CN (15 ml) was added, with stirring, to a solution of $\text{Se}(\text{SeCN})_2$ (0.30 g) in CH_2Cl_2 (30 ml). Dark brown crystals precipitated after cooling to -20°C . The crystals decompose at room temperature to a white powder

if not kept in a closed tube. Found: C 14.15; H 2.89; N 2.19; Br 62.50; Se 18.48. Calc. for $\text{C}_{18}\text{H}_{28}\text{N}_2\text{Br}_{14}\text{Se}_4$: C 12.67; H 1.65; N 1.64; Br 65.54; Se 18.50.

X-Ray structure analysis. Because of the instability of the crystals, the specimen used for X-ray measurements was sealed in a capillary tube immediately after preparation. Unit cell dimensions were determined and intensity data recorded on a CAD4 diffractometer, using graphite-monochromated $\text{CuK}\alpha$ radiation ($\lambda = 1.5418$ Å). Unit cell dimensions were determined from the diffractometer angles for 25 automatically centred reflections. Intensities out to 60° were recorded using the ω -scan mode with scan width $1.00 + 0.142 \tan\theta$, plus 25% on each side for background. Of 3001 recorded reflections, 2114 had $I > 2\sigma(I)$ and were used in the calculations. The intensities were corrected for Lorentz and polarization effects and for decay. Maximum decay correction, based on three reference reflections measured every 90 min of exposure time, was 10%. The crystal shape was not well defined and because of this and, in part, the presence of the capillary tube its dimensions were difficult to

Table 1. Atomic coordinates for $[C_6H_5(CH_3)_3N]_2Se_4Br_{14}$ with e.s.d.'s in parentheses.

Atom	x	y	z	$B_{eq}/\text{\AA}^2$
Se(1)	0.24710(24)	-0.06613(18)	-0.12013(18)	2.60(5)
Se(2)	0.21038(24)	0.15422(18)	0.08894(17)	2.48(5)
Br(1)	0.35516(31)	-0.00849(23)	-0.36044(20)	4.37(7)
Br(2)	0.16253(31)	-0.29897(21)	-0.04994(23)	4.56(7)
Br(3)	0.32363(27)	0.20140(19)	-0.18080(18)	3.22(6)
Br(4)	0.12089(27)	-0.11095(20)	0.14965(19)	3.42(6)
Br(5)	0.27091(30)	0.39111(20)	0.01854(21)	4.14(7)
Br(6)	0.09666(31)	0.09010(22)	0.33063(20)	4.38(7)
Br(7)	0.51622(25)	-0.10692(18)	-0.09804(18)	2.68(5)
N	0.7675(18)	0.3750(15)	0.4372(14)	3.0(3)
C(1)	0.7631(21)	0.4521(17)	0.5115(16)	2.7(4)
C(2)	0.7016(24)	0.3961(20)	0.6528(19)	3.9(5)
C(3)	0.6866(25)	0.4747(21)	0.7162(20)	4.3(5)
C(4)	0.7318(30)	0.6100(25)	0.6489(24)	6.3(7)
C(5)	0.7903(28)	0.6661(23)	0.5146(22)	5.3(6)
C(6)	0.8102(25)	0.5942(20)	0.4451(19)	4.2(5)
C(7)	0.6192(26)	0.3754(21)	0.4122(20)	4.5(5)
C(8)	0.7820(27)	0.2340(22)	0.5153(21)	4.8(6)
C(9)	0.9000(29)	0.4314(23)	0.2980(23)	5.6(6)

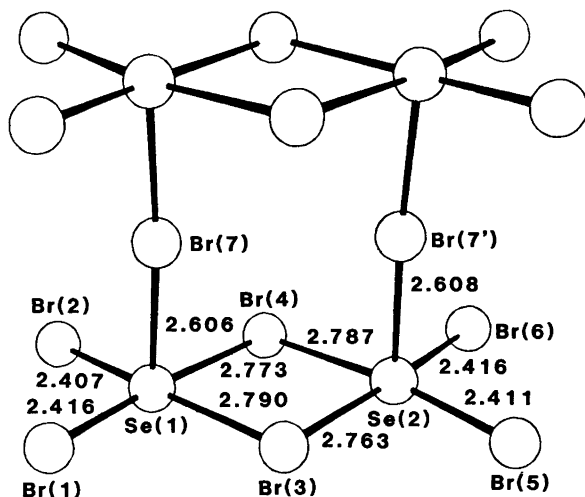
measure. An attempt to carry out absorption corrections was therefore not successful. An empirical extinction correction $F_{\text{corr}} = F_c(1+gI_c)$ was applied, and g was refined to 1.33×10^{-6} . The

calculations were carried out using the Enraf-Nonius SDP programs. Scattering factors, including anomalous dispersion terms, were taken from Ref. 3. Refinements were by full-matrix least-

Table 2. Distances (\AA) and angles ($^\circ$) in the anionic selenium-bromine species, with e.s.d.'s in parentheses.

Bond lengths			
Se(1)–Br(1)	2.416(2)	Se(2)–Br(5)	2.411(2)
Se(1)–Br(2)	2.407(2)	Se(2)–Br(6)	2.416(2)
Se(1)–Br(3)	2.790(2)	Se(2)–Br(3)	2.763(2)
Se(1)–Br(4)	2.773(2)	Se(2)–Br(4)	2.787(2)
Se(1)–Br(7)	2.606(2)	Se(2)–Br(7')	2.608(2)
Bond angles			
Br(1)–Se(1)–Br(2)	93.78(6)	Br(5)–Se(2)–Br(6)	95.18(6)
Br(1)–Se(1)–Br(3)	90.68(6)	Br(5)–Se(2)–Br(3)	90.64(5)
Br(1)–Se(1)–Br(4)	175.44(7)	Br(5)–Se(2)–Br(4)	173.19(7)
Br(1)–Se(1)–Br(7)	91.74(6)	Br(5)–Se(2)–Br(7')	93.78(6)
Br(2)–Se(1)–Br(3)	174.95(7)	Br(6)–Se(2)–Br(3)	173.84(7)
Br(2)–Se(1)–Br(4)	90.40(6)	Br(6)–Se(2)–Br(4)	88.71(5)
Br(2)–Se(1)–Br(7)	93.72(6)	Br(6)–Se(2)–Br(7')	92.48(6)
Br(3)–Se(1)–Br(4)	85.08(5)	Br(3)–Se(2)–Br(4)	85.31(5)
Br(3)–Se(1)–Br(7)	88.52(5)	Br(3)–Se(2)–Br(7')	89.14(5)
Br(4)–Se(1)–Br(7)	89.81(5)	Br(4)–Se(2)–Br(7')	91.63(5)
Se(1)–Br(3)–Se(2)	94.84(5)	Se(1)–Br(4)–Se(2)	94.67(5)
		Se(1)–Br(7)–Se(2')	175.87(6)

Fig. 1. A view of the Se₄Br₁₄²⁻ ion in the phenyltrimethylammonium salt.



squares, the sum minimized being $\Sigma w\Delta^2(F)$ with $w^{-1} = \sigma^2(F) = \sigma^2(I)/4LpI$, and $\sigma^2(I) = \sigma^2(I)_{\text{count}} + (0.02I)^2$.

An attempt was made to solve the structure by direct methods (MULTAN), but without success. The framework of the planar Se₂Br₆ group was revealed from the Patterson map, and the locations of all Se and Br atoms were then found by the method of trial and error. The C and N atoms were located from the difference electron density map. The hydrogen atoms of the phenyl group were placed geometrically at C–H = 0.95 Å. They were given a common, fixed B_{iso} and held fixed.

With anisotropic thermal parameters for Se and Br, and isotropic parameters for C and N (123 variables) the refinement converged at $R = 0.069$, $R_w = 0.084$, $S = 3.318$. Parameter shifts in the last refinement cycle were less than one per cent of the associated standard deviations. The highest peak in the final difference electron density map was 0.93 e Å⁻³. Atomic coordinates and equivalent thermal parameters are listed in Table 1. Complete lists of anisotropic thermal parameters, bond lengths and angles, and hydrogen coordinates are available from the authors upon request.

Crystal data. [C₆H₅(CH₃)₃N]₂Se₄Br₁₄, $M = 1707.0$, triclinic, space group $P\bar{1}$ (No. 2); $a = 9.247(2)$, $b = 11.162(1)$, $c = 11.680(1)$ Å, $\alpha = 64.54(1)$, $\beta = 70.13(1)$, $\gamma = 89.71(1)^\circ$, $V = 1009.5$

(3) Å³, $Z = 1$, $D_x = 2.808$ g cm⁻³; $F(000) = 776$, $\mu(\text{CuK}\alpha) = 232.6$ cm⁻¹.

Results and discussion

The Se₂Br₆²⁻ anion is known from the crystal structure of the tetraphenylphosphonium salt.⁴ It is a planar, dinuclear, di-Br-bridged complex with the two Se atoms as nuclei. The anion in the present compound, viz. Se₄Br₁₄²⁻, may be looked upon as a dinuclear complex with two Se₂Br₆²⁻ species acting as bidentate ligands and with two Br atoms, of charge + 1, as nuclei. A view of the ion is shown in Fig. 1, and bond lengths and angles are reported in Table 2.

The Se₂Br₆²⁻ ligand. As in the structure of the tetraphenylphosphonium salt,⁴ the atoms of the Se₂Br₆²⁻ groups in the present compound are very nearly co-planar. The largest deviation of an atom from a least-squares plane is 0.082 Å. Each of the two selenium atoms is bonded to two terminal bromine atoms and two bridging bromine atoms, resulting in distorted square-planar coordination. The long bonds to bridging bromine atoms are *trans* to rather short bonds to terminal bromine atoms. The variation in the lengths of the terminal Se–Br bonds, 2.407(2)–2.416(2) Å, is small but significant and the bonds are definitely longer than the Se–Br single bond, 2.31 Å. The lengths of the bridging bonds are 2.763(2)–2.790(2) Å and are thus clearly shorter than the

Table 3. Bond lengths (Å) and angles (°) of X_T -Se- X_B ^a sequences in dinuclear complexes of divalent selenium. E.s.d.'s of bond lengths are 0.002 Å.

Compound	Se- X_T	Se- X_B	(Se- X_B) -(Se- X_T)	(Se- X_B) +(Se- X_T)	X_T -SE- X_B	Ref.
[(C ₆ H ₅) ₄ P] ₂ Se ₂ Br ₆	2.399(1)	2.887(1)	0.488	5.286	176.94(2)	4
	2.485(1)	2.710(1)	0.225	5.195	173.13(2)	
[C ₆ H ₅ (CH ₃) ₃ N] ₂ Se ₄ Br ₁₄	2.407(2)	2.790(2)	0.383	5.197	174.95(7)	This work
	2.416(2)	2.773(2)	0.357	5.189	175.44(7)	
	2.411(2)	2.787(2)	0.376	5.198	173.19(7)	
	2.416(2)	2.763(2)	0.347	5.179	173.84(7)	
KSe(SeCN) ₃ ^{1/2} H ₂ O	2.403(2)	3.244(2)	0.841	5.647	173.06(5)	10
	2.419(2)	3.089(2)	0.670	5.508	170.58(6)	
	2.411(2)	3.167(2)	0.756	5.578	172.81(5)	
	2.395(2)	3.207(2)	0.812	5.602	174.94(5)	
RbSe(SeCN) ₃ ^{1/2} H ₂ O	2.406(2)	3.331(2)	0.925	5.737	170.69(6)	11
	2.409(2)	3.127(2)	0.718	5.536	173.20(6)	
	2.393(2)	3.255(2)	0.862	5.648	172.64(6)	
	2.391(2)	3.272(2)	0.881	5.663	172.60(6)	
KSe(SCN) ₃ ^{1/2} H ₂ O	2.252(2)	3.112(3)	0.860	5.364	168.89(10)	14
	2.282(3)	2.953(3)	0.671	5.235	171.38(10)	
	2.318(3)	2.906(3)	0.588	5.224	175.31(9)	
	2.290(2)	2.907(3)	0.617	5.197	176.26(11)	

^a X_T : Terminal Br, Se or S; X_B : Bridging Br, Se or S.

van der Waals distances of closest approach. The angles of the four nearly linear Br-Se-Br systems are 173.19(7)–175.47(7)°. From the geometry of the present ligand and that of the corresponding ion in the tetraphenylphosphonium salt, and from the lengths of the Se-Br bonds, the three-centre, four-electron, 3c-4e bonding model will fit well. Table 3 gives the bond lengths and angles for X-Se-X systems found in crystal structures of dinuclear complexes of divalent selenium. When X is SeCN or SCN, the chalcogen is the complexing atom. It is seen from Table 3 that the dimensions of the Se₂Br₆²⁻ anion do not show any appreciable change when the ion is coordinated to bromine. Asymmetry in the bonds is found in all the complexes. The asymmetry is clearly less for bromides than for chalcogens as ligands. Asymmetry in 3c-4e bonding has been discussed by Foss,⁵ who concludes that the total length of the system will increase with increasing asymmetry. The length of the linear Br-Se-Br sequence in compounds with a symmetric or a nearly symmetric system is 5.150(1) Å in tetramethylammonium dibromocyanoselenate(II),⁶

5.196(1) Å in tetraphenylphosphonium tetrabromoselenate(II)⁴ and 5.189(3) Å in dibromo-(tetramethylthiourea)selenium(II).⁷ In the present structure the asymmetries, i.e. the differences between the two Se-Br bond lengths, show only small variations, and the mean value is 0.366 Å. Since the mean value of the length of the four Br-Se-Br systems is 5.184 Å, the moderate asymmetry seems to have a rather small lengthening effect on the sequence.

From the crystal structures mentioned above and from structures with symmetric, linear Se-Se-Se⁸⁻⁹ or Cl-Se-Cl⁶ sequences, it seems that chlorine and bromine have relatively stronger bonds to divalent selenium than selenium and, with more uncertainty, sulfur.

Coordination at the central bromine atoms. A tendency of the central selenium atom in a square-planar arrangement to participate in a fifth coordination has been found in the dimerized seleniumtriselenocyanate ion, Se₂(SeCN)₆²⁻, in its potassium and rubidium salts.¹⁰⁻¹¹ The central selenium atoms act as donors in the fifth, out

of plane, direction. In the present structure the selenium atoms are, in addition to being central atoms with square-planar coordination, bonded to bromine in linear, symmetrical Se–Br–Se sequences with Br–Se bond lengths of 2.607 Å. Compared with the covalent bond length of 2.357(2) Å in α-Se₂Br₂¹² or 2.368(1) Å in β-Se₂Br₂, and with the Br–Br bond length of 2.551(2) Å¹³ in symmetrical 3c–4e Br₃[–] systems or with Se–Br lengths in linear Br–Se–Br systems mentioned above, the Se–Br–Se sequence in the present structure must be of the 3c–4e type.

The dimensions of the phenyltrimethylammonium ion are: N–C = 1.454(13)–1.521(16) Å, C–C = 1.314(19)–1.423(16) Å, C–N–C = 106.7(10)–113.9(10)°. The ion does not have any close contacts of particular interest.

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