1,2,3-Triselenetan-4-(*Se*,*Se*-dibromoselone); CBr_2Se_4.
# Crystal Structure and Mechanism of Formation

SINE LARSEN [a] and LARS HENRIKSEN [b]

[a] Department of Physical Chemistry and [b] Department of General and Organic Chemistry, University of Copenhagen, H.C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

The title compound is formed by a bromide ion catalyzed reaction between carbon diselenide and diselenium dibromide. The crystal structure of CBr_2Se_4 was determined from X-ray diffraction data. The crystals are orthorhombic, space group $Pna2_1$ with cell dimensions $a=21.169(11)$ Å, $b=4.176(2)$ Å, $c=8.496(4)$ Å, $Z=4$. Based on 1153 observed reflections the final R-value is 0.028. The CBr_2Se_4 moiety is planar with the overall symmetry close to C_{2v}. In CBr_2Se_4 three different types on environment are observed for the Se atoms. The three similar C−Se bonds have an average bond length 1.847 Å. The two Se−Se bonds are similar to the bonds in elementary Se. The Br−Se−Br fragment is linear. The structure of CBr_2Se_4 appears to be strongly stabilized by short intermolecular interactions between Se and Br.

The kinetics of the formation of CBr_2Se_4 indicate that diselenium dibromide is converted by bromide ion into a bromodiselenide ion which attacks carbon diselenide in the rate determining step. The different surroundings for the two Br atoms and the preferred directions of crystal growth suggest that the crystal is formed from $CBrSe_4^+$ Br^- ion pairs.

The synthesis of selenoureas from carbon diselenide, bromide and amines has recently been described by one of us.[1] This preparative route fails for some amines when very bulky side chains and other reactions occur. With *tert*-butylamine bronze coloured crystals were formed in a slow reaction. An elemental analysis showed that the composition of the crystals is CBr_2Se_4. It was subsequently found that CBr_2Se_4 could be obtained in virtually quantitative yield by a bromide ion catalyzed reaction between carbon diselenide and diselenium dibromide.

$$CSe_2 + Se_2Br_2 \xrightarrow{\;Br^-\;} CBr_2Se_4$$
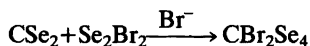
The crystals of CBr_2Se_4 are air-stable and have been stored for more than a year at room temperature without any appreciable change. They are thermally stable up to 185 °C at which temperature the crystals decompose forming selenium and volatile substances. CBr_2Se_4 is almost insoluble in all common solvents. When it is dissolved, *e.g.* in boiling dimethylformamide, extensive degradation occurs.

The presence of a selenocarbonyl structural unit in CBr_2Se_4 was indicated by its reaction with piperidine forming selenocarbonyl-bis-piperidine according to the following reaction.

$$CBr_2Se_4 + 4C_5H_{10}NH \rightarrow$$

$$(C_5H_{10}N)_2CSe + 3Se + 2C_5H_{10}NH_2^+ + 2Br^-$$

$$(79\ \%)$$
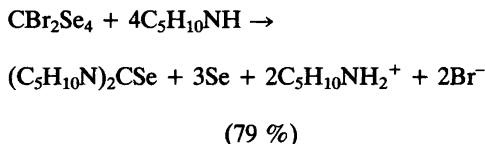
These conspicuous properties of CBr_2Se_4 initiated a more detailed examination of the compound. The present paper describes the results of the crystal structure determination and the study of the kinetics and mechanism of the formation of CBr_2Se_4 which can be given the systematical name 1,2,3-triselenetan-4-(*Se*,*Se*-dibromoselone).

EXPERIMENTAL

Crystallographic examination. It is impossible to recrystallize CBr_2Se_4 but the crystals formed by precipitation from the reaction between carbon diselenide and diselenium dibromide in dibromomethane were of sufficient quality for the X-ray diffracton investigation. The compound crystallizes as brown plates with (100) as the plate face. Preliminary Weissenberg and precession photographs showed that the crystals are orthorhombic. The systematically absent reflections $0kl:k+l=2n+1$, $h0l:h=2n+1$ indicated the possible space groups $Pna2_1$ and $Pnam$. A single crystal bounded by the planes (201) (100) and ($\bar{2}$10) of a size $0.083\times0.40\times0.35$ mm along the axial directions was selected for the collection of intensity data and for the determination of accurate cell parameters. These measurements were performed at 296 K using a Picker FACS-1 diffractometer with monochromatized $MoK\alpha$ radiation. The setting angles for 24 reflections were optimized automatically and used in a least squares refinement of the unit cell parameters and the orientation matrix. The diffractometer was operated in the $\omega-2\theta$ scan mode at a rate of 1°/min in 2θ. The scan was from $2\theta_l=2\theta_0-1.2-0.231\tan\theta^\circ$ to $2\theta_h=2\theta_0+1.5+0.462\tan\theta^\circ$ where $2\theta_0$ is the calculated peak position. Background counts were made for 20 s at each end of the scan range.

The intensities of 5 standard reflections measured after every 50 reflections all decreased *ca* 12 % during the data collection. The decay was linear with exposure time. The reflections *hkl* and *hk-l* were measured to a maximum 2θ of 50°. The diffraction data were corrected for the degradation by a function linear in exposure time, and for Lorentz, polarization and absorption effects. The latter correction was performed by a Gaussian integration procedure with a $12\times16\times16$ grid.[2] The transmission factors were in the range $0.0123-0.1198$. The reflections were averaged according to the point symmetry *mm2* resulting in 1296 reflections of which the 1153 with $|F|^2\geq2\sigma(|F|^2)$ were classified as observed and used in the subsequent structure determination and refinement.

During the crystallographic calculations use was made of the following computer programs: the Vanderbilt system[3] for diffractometer operations, a data-reduction program of local origin based on DATAP,[2] MULTAN[4] and the X-RAY system[5] for the structure solution and refinement and ORTEP II[6] for the illustrations. The scattering factors used were those of Cromer and Mann.[7] The anomalous dispersion corrections added to the scattering factors for Se and Br were

calculated by Cromer and Liberman.[8]

Stock solutions for preparations and kinetic experiments. A. Diselenium dibromide (0.2 M in dichloromethane) was prepared by stirring selenium (6.316 g) with bromine (6.392 g) in dichloromethane (20 ml) until all of the selenium had dissolved and then diluting to 200 ml.

B. Carbon diselenide[9] (0.2 M in dichloromethane).

C. Tetrabutylammonium bromide (0.04 M in dichloromethane).

Preparation of CBr_2Se_4 1,2,3-triselenetan-4-(Se,Se-dibromoselone). Solutions A (45 ml), B (40 ml) and C (10 ml) were mixed and left in a stoppered flask for 3 d at room temperature. Precipitated material was filtered off, washed with dichloromethane and dried to give CBr_2Se_4 (3.74 g, 7.67 mmol; yield 96 % based upon carbon diselenide). Elemental analyses: Found: 2.58 % C, 32.40 % Br; calc. for CBr_2Se_4: 2.46 % C, 32.79 % Br. I.R. [$4000-200$ cm^{-1}; CsBr−disc): 873(s), 844(w), 339(m), 300(w), 274(m), 261(m), 200(s)].

Reaction of CBr_2Se_4 with piperidine. Piperidine (10 mmol) was added to a suspension of CBr_2Se_4 (2.0 mmol) in trichloromethane (10 ml). The mixture was irradiated with ultrasound in a 30 W laboratory cleaning bath for 1 h and then filtered. The filtrate was worked up according to Ref. 1 to give selenocarbonyl-bis-piperidine (1.59 mmol, 79 %), identical (m.p., mixed m.p.) with an authentic[1] sample.

Kinetic investigations. Stock solutions A, B and C were mixed and diluted with dichloromethane to a total of 10 ml. These solutions were placed in stoppered, balanced centrifugation tubes and left at 21 °C for the desired length of time. Precipitated material was isolated by centrifugation and decantation of the supernatant, washed twice with dichloromethane in the same manner, dried and determined gravimetrically. Samples were taken to cover $20-95$ % conversion of carbon diselenide. Initial concentrations were within the ranges (mol/l) $0.01\leq C_{CSe_2}\leq0.04$, $0.03\leq C_{Se_2Br_2}\leq0.12$ and $0.001\leq C_{Br}-\leq0.024$.

CRYSTAL DATA

1,2,3-Triselenetan-4-(*Se,Se*-dibromoselone), CBr_2Se_4, orthorhombic, $a=21.169(11)$ Å, $b=4.176(2)$ Å, $c=8.496(4)$ Å, $V=751.0$ Å^3, $d_x=4.313$ g/cm^3, $Z=4$. $\mu(MoK\alpha)=284$ cm^{-1}, $F(000)=848$. Systematically absent reflections: $0kl$ when $k+l=2n+1$, $h0l$ when $h=2n+1$. Space group $Pna2_1$.

Table 1. Final fractional atomic coordinates and equivalent isotropic temperature factors $U_{eq}{}^a$ ($\text{Å}^2 \times 10^2$).

Atom	x	y	z	U_{eq}
C	0.8799(4)	0.577(2)	0.2494(11)	2.4(5)
Se1	0.80080(5)	0.3924(3)	0.2402(2)	2.92(5)
Se2	0.81006(5)	0.3667(3)	0.5182(2)	3.45(6)
Se3	0.90851(5)	0.6038(3)	0.4517(2)	3.13(5)
Se4	0.92499(5)	0.7205(3)	0.0735(2)	2.83(5)
Br1	1.01383(5)	0.8905(3)	0.25000	3.63(6)
Br2	0.83020(5)	0.5286(3)	-0.1006(2)	4.11(6)

^{a} $U_{eq}=\frac{1}{3}\sum_j\sum_i U_{ij}a_i^*a_j^*\bar{a}_i\cdot\bar{a}_j.$

STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by direct methods. A standard run of MULTAN[4] assuming the space group $Pna2_1$ gave starting positions for the six heavy atoms. As it was not possible with certainty at this stage to establish their chemical identity they were all introduced as Se atoms. A difference density calculated after an isotropic refinement revealed the position for the carbon atom. After this atom was included in the refinement it was possible to distinguish between the Se and Br atoms in the structure from the differences in their thermal parameters. The structure was refined by the method of least squares minimizing $\Sigma w||F_o|-|F_c||^2$, using anisotropic thermal parameters and the weights, $w^{-1}=(2.5\sigma^2(F)+0.0015F^2)$. The opposite polarity of the crystal could be rejected at a significance level less than 10^{-6} by Hamiltons R-value test performed as described by Rogers.[10] The final weighted and unweighted residuals

$$R_w=\left\{\frac{\Sigma w(|F_o|-|F_c|)^2}{\Sigma w|F_o|^2}\right\}^{\frac{1}{2}} \text{ and } R=\frac{\Sigma||F_o|-|F_c||}{\Sigma|F_o|}$$

were 0.028 and 0.033 respectively. In the final cycle of least squares refinement the maximum shift of parameters was 0.03σ. The maximum peak in a final difference density map is 1.1 e/Å^3.

The final positional parameters and equivalent isotropic temperature factors are given in Table 1. The anisotropic thermal parameters and lists of observed and calculated structure amplitudes may be obtained upon request from the authors.

DESCRIPTION OF THE STRUCTURE

The structure of the molecular building unit CBr$_2$Se$_4$ is illustrated by the ORTEP drawing in Fig. 1. The many short intermolecular distances in the structure (*vide infra*) make it likely that they are important for the stability of the CBr$_2$Se$_4$ molecule. The bond lengths and bond angles are given in Table 2. The atomic distances to the least squares plane listed in Table 3 show that the CBr$_2$Se$_4$ moiety is planar. The angles between the normal to the least squares plane and the a, b and c axis are 65, 155 and 95° respectively, making the molecules almost parallel to the c-axis.

From inspection of the bond angles and bond distances it seems legitimate to describe the over-all symmetry of the molecule as C_{2v}. The three Se$-$C bonds are almost identical
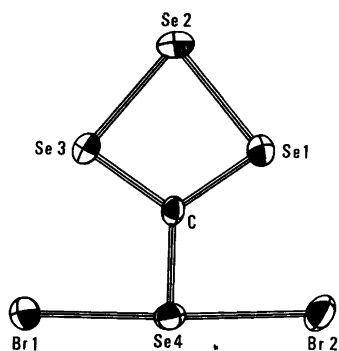

Fig. 1. CBr$_2$Se$_4$ seen perpendicular to the molecular plane showing the atomic labelling.

Table 2. Bond lengths (Å) and bond angles (°) with ESD's.

Se1–Se2	2.373(2)	Se2–Se3	2.376(2)
Se1–C	1.844(9)	Se3–C	1.826(10)
Se4–Br2	2.619(2)	Se4–Br1	2.508(2)
C–Se4	1.872(1)		
Se1–Se2–Se3	79.44(6)	Se1–C–Se3	111.5(5)
Se2–Se1–C	84.4(3)	Se2–Se3–C	84.7(3)
Se1–C–Se4	124.3(5)	Se4–C–Se3	124.2(5)
C–Se4–Br2	87.8(3)	C–Se4–Br1	89.8(3)
Br1–Se4–Br2	177.5(3)		

$\langle Se-C \rangle = 1.847$ Å and similar to the Se–C bond in N-tetramethylselenourea, 1.836(4) Å[11] and the short Se–C bonds in selenium (1-pyrrolidinecarbodiselenoate), of 1.841(6) Å[12]. Considering the planar environment of the C-atom and the magnitude of the Se–C–Se angles the arrangement around the carbon atom in CBr_2Se_4 is similar to a C in a triselenocarbonate ion. The

Table 3. Distances (Å) from the least squares plane in CBr_2Se_4.

C	0.005
Se1	0.009
Se2	−0.013
Se3	0.009
Se4	−0.013
Br1	0.002
Br2	0.001

two Se–Se bonds are identical in magnitude; 2.373(2) and 2.376(2) Å. They are slightly longer than the Se–Se distances observed in elementary Se,[13] $\langle 2.334(5) \rangle$ Å and slightly shorter than the long Se–Se distances found in the Se_{10}^{2+} ion.[14]

The values observed for the Se–Se–Se angle and C–Se–Se angles are similar to those found in the structure of selenium bis(1-pyrrolidinecarbodiselenoate).[12] The two Se4–Br distances are slightly but significantly different and represent the deviation from the C_{2v} symmetry in the molecule. The Se–Br distances are similar to those found in $(H_5O_2)_2$ $SeBr_6$,[15] which also has the Br–Se–Br system in a linear arrangement $\langle Se-Br \rangle = 2.565$ Å. The planarity of the molecule leads to short intramolecular contacts between Se3–Br1 and Se1–Br2 of 3.056(2) and 3.015(3) Å respectively.

Only the eight intermolecular distances given in Table 4. are shorter than the sum of the van

Table 4. Intermolecular Distances (Å) and angles (°) in CBr_2Se_4. θ is the angle between the interatomic vector and the normal to the molecular plane.

		θ		
Se1–Br2[a]	3.439(2)	88.0	C–Se1–Br2[a]	154.1(3)
Se2–Br2[a]	3.439(2)	87.9	Se3–Se2–Br2[a]	149.17(7)
Se2–Br2[b]	3.336(3)	102.3	Se1–Se2–Br2[b]	165.45(7)
Se4–Br1[c]	3.436(2)	101.7	C–Se4–Br1[c]	168.4(3)
Se1–Se2[d]	3.604(2)	136.5	C–Se1–Se2[d]	112.6(3)
Se1–Se2[e]	3.726(2)	71.7	C–Se1–Se2[e]	147.0(3)
Se3–Br1[f]	3.686(2)	113.1	C–Se3–Br1[f]	146.2(3)
Se3–Br1[g]	3.659(2)	50.1	C–Se3–Br1[g]	140.0(3)
			Se2[e]–Se1–Se2[d]	69.45(5)
			Br1[f]–Se3–Br1[g]	69.30(5)

a: $1\frac{1}{2}-x$, $y-\frac{1}{2}$, $\frac{1}{2}+z$; *b:* x,y, $1+z$; *c:* $2-x$, $2-y$, $z-\frac{1}{2}$ *d:* $1\frac{1}{2}-x$, $\frac{1}{2}+y$, $z-\frac{1}{2}$; *e:* $1\frac{1}{2}-x$, $y-\frac{1}{2}$, $z-\frac{1}{2}$; *f:* $2-x$, $2-y$, $\frac{1}{2}+z$; *g:* $2-x$, $1-y$, $\frac{1}{2}+z$.
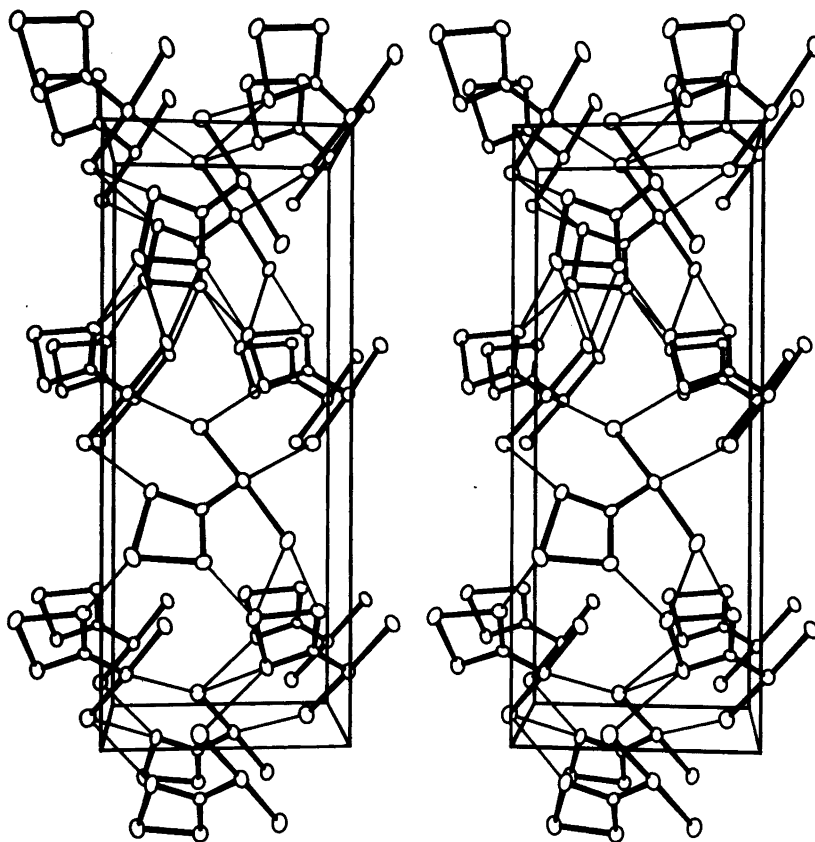
Fig. 2. Stereo pair of the packing in CBr$_2$Se$_4$ viewed along *b*. The inter-molecular contacts smaller than the sum of the van der Waals radii [16] are indicated by the open bonds.

der Waals radii [16] ($d_{v.d.w}$(Se−Se)=3.80 Å, $d_{v.d.w}$(Se−Br)=3.75 Å). They fall into two groups, four short ~3.4 Å and four long ~3.7 Å. These intermolecular interactions are shown on the stereo pair in Fig. 2, which illustrates the molecular packing. The interatomic distances between the molecules related by translational symmetry along the short *b*-axis are in the range 3.85−4.30 Å and they are all slightly longer than the sum of the corresponding van der Waal radii. The planar trapezoid four-coordination around Se2 with two short covalent bonds and two longer intermolecular distances is similar to the structural arrangement around Se(II) in selenium bis(diethyldiselenophosphinate),[17] a coordination type that Brøndmo, Esperås and Husebye [18] described as class II.

The intermolecular interactions between Se1 and Se2 are similar to those between Se3 and Br1

with respect to distances and the Se2−Se1−Se2 and Br1−Se3−Br1 angles. Se1 has one additional shorter contact to Br2, but apart from that the environments of Se1 and Se3 are very similar. The three covalent bonds to Se4 and the short contact distance Se4−Br1 are coplanar and almost at right angles, a similar arrangement is found for Te in phenyl bis(thiourea)tellerium(II) chloride.[19] Based primarily on the differences in structural environment it could be stated that CBr$_2$Ce$_4$ contains three types of Se atoms in agreement with the apparent C_{2v} symmetry of the molecule.

Br1 and Br2 are involved in different inter-molecular interactions. Br2 has three short contact distances where Br1 has one short and two longer. These differences could explain why the Se4−Br2 bond, 2.614 Å is significantly longer than the Se4−Br1 bond, 2.503 Å.

The packing arrangement is strongly influenced by interactions between Se and Br. Rosenfield, Pathasarathy and Dunitz[20] examined the directional preference of non-bonded atomic contacts between divalent sulfur and nucleophiles and found that nucleophiles tend to approach S approximately along the extension of one of the covalent bonds to S. To investigate if the Se−Br nonbonded contacts in this structure fit into a similar scheme, the angle, θ, between the perpendicular to the molecular plane and the vector specifying the Se−Br non-bonded distance was calculated. These angles are also listed in Table 4. The four short non-bonded Se−Br contacts have azimuth angles close to 90° and are trans to one of the covalent bonds the same arrangement Rosenfield, Pathasarathy and Dunitz found for the similar sulfur-nucleophile interactions. The equivalent angles for the four longer non-bonded interactions do not reveal any systematic behaviour. The great similarity between the four short non-bonded Se−Br contacts and the S to nucleophile contacts could indicate that the short Se−Br contacts are due to interactions of the nucleophilic bromine with the lowest unoccupied molecular orbital (LUMO) with σ symmetry.

KINETICS AND MECHANISM

As described in the experimental part, carbon diselenide and diselenium dibromide give CBr_2Se_4 almost quantitatively in the presence of bromide ion. Since both of the former reagents are electrophiles it is likely that the bromide ion acts as a nucleophilic activator. The nucleophilic reagent formed could be envisaged to be either bromodiselenide ion ($BrSeSe^-$) or bromodiselenoformate ion ($Br-CSe_2^-$).[77] Se NMR experiments in $CDCl_3$ showed that the signal (1161.14 ppm) of diselenium dibromide was scrambled by bromide ion indicating a moderately rapid exchange process. The signal from carbon diselenide (299.8 ppm) was unaffected by the presence of bromide ion. On this basis we find it justified to assume that the $BrSeSe^-$ ion is formed by the attack of Br^- and that this ion acts as the nucleophilic reaction partner.

A kinetic investigation carried out under pseudo-order conditions with carbon diselenide as the limiting reagent showed 1) that the rate of formation of CBr_2Se_4 followed 1. order kinetics with respect to carbon diselenide and 2) that the observed 1. order rate constants, k_{obs}, depended on the concentration of diselenium dibromide as well as that of bromide ion. Fig. 3 shows the quantity $k'=k_{obs} \cdot C_{Se_2Br_2}^{-\frac{1}{2}} \cdot C_{Br^-}^{-1}$ as a function of the ratio $r=C_{Se_2Br_2}^{\frac{1}{2}} \cdot C_{Br^-} \cdot C_{CSe_2}^{-1}$. For $r > ca.$ 0.1 a constant value of $k'=1.07\pm0.06$ min^{-1}M$^{-3/2}$ was obtained while below $r=0.1$ a systematic increase of k' with decreasing values of r was observed.

The results for high values of r suggest that the active nucleophile is formed, together with an additional species, from one mole of diselenium dibromide and two moles of bromide ion and that the subsequent reaction of this nucleophile with carbon diselenide is the rate determining step. It is further indicated that the equilibrium concentration of nucleophile is very low since the stoichiometric concentrations of reagents suc-
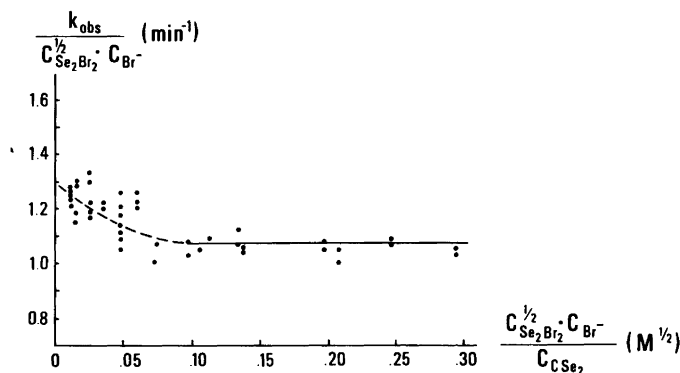

Fig. 3. The rate of formation of CBr_2Se_4 as a function of the ratio of intermediate to carbon diselenide concentrations. $C_{Se_2Br_2}$ is the average between the initial and end concentrations.

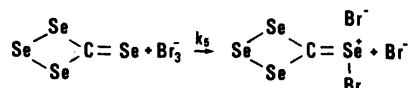$$Br_2Se_2 + Br^- \rightleftharpoons Br-Se-Se^- + Br_2 \qquad K_1 = \frac{[Br\,Se_2^-][Br_2]}{[Br_2Se_2][Br^-]}$$

$$Br_2 + Br^- \rightleftharpoons Br_3^- \qquad K_2 = \frac{[Br_3^-]}{[Br_2][Br^-]}$$

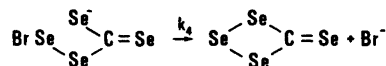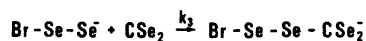$$Br-Se-Se^- + CSe_2 \xrightarrow{k_3} Br-Se-Se-CSe_2^-$$
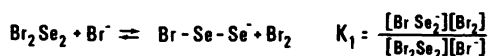

Fig. 4. Tentative mechanism for the formation of CBr$_2$Se$_4$.

cessfully reproduces actual concentrations.

A tentative mechanism in accord with the preceding observations in shown in Fig. 4. It is suggested (1) that BrSeSe$^-$ and bromine are formed in an equilibrium reaction (K_1) from diselenium dibromide and bromide ion, (2) that the concentration of bromine is regulated by a second equilibrium with bromide ion to give tribromide ion (K_2) and (3) that the reaction of BrSeSe$^-$ with carbon diselenide (k_3) constitutes the rate determining step. This mechanism requires the rate d [CBr$_2$Se$_4$]/dt=k_3[CSe$_2$][BrSeSe$^-$] where [BrSeSe$^-$] is given by [BrSeSe$^-$]= K_1K_2[Se$_2$Br$_2$][Br$^-$]^2[Br$_3^-$]$^{-1}$. With the implicit assumption $K_1 \ll K_2$ the concentration of free bromine is negligible and [Br$_3^-$]=[BrSeSe$^-$]. This leads to the rate expression:

$$d\,[CBr_2Se_4]/\,dt = k_3(K_1K_2)^{\frac{1}{2}}C_{Se_2Br_2}^{\frac{1}{2}}C_{Br^-}\,[CSe_2]$$

in accord with the experimental results. The systematic increase of k' observed for r-values below 0.1 indicates that the pre-equilibrium approximation employed above, breaks down so that a steady-state model ought to be applied to the concentration of BrSeSe$^-$ in this region.

The kinetics gives no information beyond this point and the subsequent reaction steps must remain largely speculative. The postulation of a cyclization of 2-bromodiselan-1-diselenocarboxy-late into 1,2,3-triselenetan-4-selone (k_4) followed

by the reaction of the latter with bromine (k_5) in two fast steps are, however, precedented, as the reaction of selenyl bromides (RSeBr) with sele-nols or selenolate ions to give diselenides[21] as well as that of selones with bromine to give Se,Se-dibromides[22] are described as fast reactions at room temperature. The formulation of the ultimate step leading to crystalline CBr$_2$Se$_4$ (k_6) as an association of ion-pairs (or ion-aggregates) is corroborated by a scrutiny of the crystal structure. The two bromine atoms are slightly but significantly different with respect to intra- and intermolecular coordination distances. The six nearest neighbours to Br1 are two intramolecular contacts to Se4 and Se3, one short intermolecular distance to Se4 and two short distances to Se3 in neighbouring stacks and finally one contact to Se4 (3.958 Å) in the same stack. The last distance is larger than the sum of the van der Waals radii and is not shown in Table 4. This pattern is reminiscent of the coordination of an anion in an ion-cluster to positive sites in the surrounding cations. In contrast Br2 have three short intermolecular contacts to Se1 and Se2 in two units in a neighbouring stack. These interactions could indicate that Br2 is attracted to the region of high electron density on the outside of the Se1−Se2 bond and suggests that Br2 originates from an electrophilic structural element, cf. the function of bromine as an electrophilic center in Se$_2$Br$_2$ (Fig. 4 step 1).

Another feature which supports the ion-pair mechanism is that the optimum directions for crystal growth are along the b and c axes where additional ion-pairs are readily fitted to the structure forming a sandwich consisting of two layers of cations surrounding a planar arrangement of bromide ions. Growth in the a direction requires that two triselenetan units are fitted 'back to back'. Finally it is worth noticing that the negligible solubility of CBr$_2$Se$_4$ in polarizable solvents, e.g. CHBr$_3$, combined with the finding that it dissolves (with decomposition) in more ionizing solvents, e.g. DMF, also points to the intervention of ion-pairs in the dissolution.

REFERENCES

1. Henriksen, L. Synthesis (1982) 773.
2. Coppens, P., Leiserowitz, L. and Rabino-witch, D. Acta Crystallogr. 18 (1965) 1035.
3. Lehnert, P. G. J. Appl. Crystallogr. 8 (1975) 568.

4. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A 27* (1971) 368.
5. Stewart, J. M., Ed., *The X-Ray System* Technical Report TR-446, Computer Science Center, University of Maryland, College Park 1976.
6. Johnson, C. K. *ORTEP: A Fortran Ellipsoid Plot Program for Crystal Structure Illustrations,* Report ORNL-3794, Second. Rev., Oak Ridge National Laboratory, Oak Ridge 1970.
7. Cromer, D. T. and Mann, J. B. *Acta Crystallogr. A 24* (1968) 321.
8. Cromer, D. T. and Liberman, D. *J. Chem. Phys. 53* (1970) 1891.
9. Henriksen, L. and Kristiansen, E. S. S. *Int. J. Sulfur Chem. A 2* (1972) 133.
10. Rogers, D. *Acta Crystallogr. A 37* (1981) 734.
11. Anthoni, U., Borch, G., Larsen, S. and Nielsen, P. H. *To be published.*
12. Esperås, S., Husebye, S. and Rolandsen, Å. *Acta Chem. Scand. A 29* (1975) 608.
13. Foss, O. and Janickis, V. *J. Chem. Soc. Dalton Trans.* (1980) 620.
14. Burns, R. C., Chan, W. L., Gillespie, R. J., Luk, W. C., Sawyer, J. F. and Slim, D. R. *Inorg. Chem. 19* (1980) 1432.
15. Krebs, B. and Hein, M. *Z. Naturforsch. Teil B 34* (1979) 1666.
16. Bondi, A. *J. Phys. Chem. 68* (1964) 441.
17. Husebye, S. and Helland-Madsen, G. *Acta Chem. Scand. 23* (1969) 1398.
18. Brøndmo, N. J., Esperås, S. and Husebye, S. *Acta Chem. Scand. A 29* (1975) 93.
19. Hauge, S., Johannesen, Ø. and Vikane, O. *Acta Chem. Scand. A 32* (1978) 901.
20. Rosenfield, R. E., Parthasarathy, R. and Dunitz, J. D. *J. Am. Chem. Soc. 99* (1977) 4860.
21. Rheinboldt, H. and Giesbrecht, E. *Chem. Ber. 85* (1952) 357.
22. Bodelsen, M., Borch, G., Klæboe, P. and Nielsen, P. H. *Acta Chem. Scand. A 34* (1980) 125.

Received October 3, 1983.