

Syntheses and Crystal Data on Salts of the Triselenocyanate and Seleniumtriselenocyanate Ions

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The triselenocyanates, $\text{K}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, $\text{Rb}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, $\text{Cs}(\text{SeCN})_3$, and $(\text{CH}_3)_4\text{N}(\text{SeCN})_3$, have been prepared from aqueous solutions of the corresponding selenocyanates by oxidation with bromine dissolved in benzene. The three alkali salts have also been prepared from selenium diselenocyanate, $\text{Se}(\text{SeCN})_2$, by reaction with aqueous alkali cyanide. The potassium salt has, furthermore, been prepared from selenium dicyanide, $\text{Se}(\text{CN})_2$, and aqueous potassium selenocyanate.

The seleniumtriselenocyanates, $\text{KSe}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, $\text{RbSe}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, and $\text{CsSe}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, have been prepared from selenium diselenocyanate, $\text{Se}(\text{SeCN})_2$, and aqueous alkali cyanide under conditions differing slightly from those used for the preparation of the triselenocyanates.

Unit cell and space group data on the above salts, and on CsSeCN and $(\text{CH}_3)_4\text{NSeCN}$ are given.

Improved methods are described for the preparation of selenium diselenocyanate and selenium dicyanide.

As part of a study of linear three-selenium systems, salts of the triselenocyanate ion, $(\text{SeCN})_3^-$, and of the seleniumtriselenocyanate ion, $\text{Se}(\text{SeCN})_3^-$, have been prepared. The structure of the triselenocyanate ion in the potassium and rubidium salts have been determined by X-ray methods.^{1,2}

The salts were prepared by oxidation of selenocyanate ion with bromine, or by reaction of selenium diselenocyanate with cyanide ion. Potassium triselenocyanate was also prepared from selenium dicyanide and potassium selenocyanate.

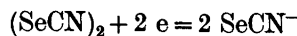
OXIDATION PRODUCTS OF THE SELENOCYANATE ION

Verneuil,³⁻⁵ in 1884-1886, described the following oxidation products of the selenocyanate ion: potassium triselenocyanate, $\text{K}(\text{SeCN})_3$, potassium seleniumtriselenocyanate hydrate, $\text{KSe}(\text{SeCN})_3 \cdot \text{H}_2\text{O}$, and selenium diselenocyanate. We find that both of the potassium salts crystallize with half a mol of crystal water, and are thus hemihydrates. Kypke and Neger⁶ in 1860

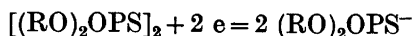
probably isolated one or both of the potassium salts, but did not determine the compositions. Cesium triselenocyanate, $\text{Cs}(\text{SeCN})_3$, was obtained in 1925 by Birckenbach and Kellermann.⁷ Potassium seleniumtriselenocyanate has, after Verneuil, been observed and analyzed by Hagelberg⁸ and by Muthmann and Schröder,⁹ in 1890 and 1900. Selenium diselenocyanate has often been prepared,⁹⁻¹⁵ and its dipole moment,¹³ crystal structure,¹⁴ and infrared spectrum¹⁵ have been reported.

The selenocyanate ion, SeCN^- , is a pseudo-halide; its oxidative dimerization product, selenocyanogen, is a pseudo-halogen. The latter, $(\text{SeCN})_2$, was isolated by Birckenbach and Kellermann¹⁶ in 1925 as a yellow crystalline powder. It has also been studied in solutions.^{7,10,15-17} Like a halogen adds halide ion, selenocyanogen adds selenocyanate ion, to give triselenocyanate ion.⁷

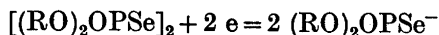
The standard redox potential of the selenocyanogen-selenocyanate couple:



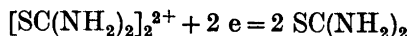
may be estimated as approximately 0.6 V, on the basis of the value, 0.77 V, determined by Bjerrum and Kirschner¹⁸ for the thiocyanogen-thiocyanate couple, and a probable difference of about -0.2 V between the two: the difference between the standard potentials for:



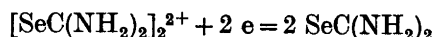
and



where R is alkyl, is 0.19 V,¹⁹ and the difference between:

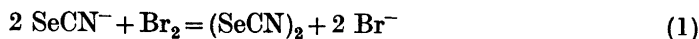


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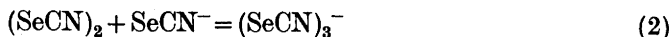


is 0.18 V.^{20,21}

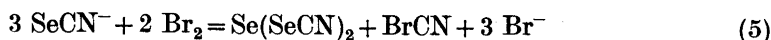
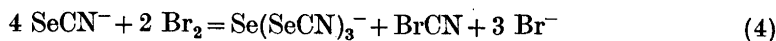
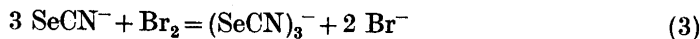
Thus, the reaction:



should go completely to the right, and in presence of excess of selenocyanate ion, triselenocyanate ion should form:



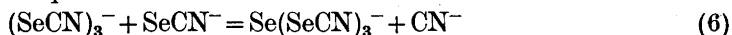
It was found that bromine dissolved in benzene, acting on a concentrated aqueous solution of an alkali or tetramethylammonium selenocyanate, was a convenient system for oxidizing selenocyanate ion. Depending on the conditions and relative amount of bromine used, three products could be isolated: triselenocyanates, seleniumtriselenocyanates, or selenium diselenocyanate. The reactions may tentatively and summarily be formulated as:



The cyanogen bromide probably hydrolyzes, or reacts with selenocyanate ion to give selenium dicyanide.

The alkali salts and tetramethylammonium salt of the triselenocyanate ion, when prepared according to eqn. (3), and crystallized at about 3°C, gave satisfactory analyses for selenium. However, if the reaction mixture was not placed in a refrigerator, but left at room temperature, a mixture of triselenocyanate and seleniumtriselenocyanate salts usually crystallized.

This indicates an equilibrium in solution:

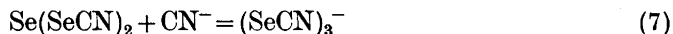


which may be pictured as a simple ligand exchange at the middle selenium atom of the complex ion.

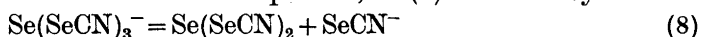
The equilibrium, (6), is demonstrated directly, later in this work, through the reaction of potassium triselenocyanate with a concentrated aqueous solution of potassium selenocyanate.

Pure samples of seleniumtriselenocyanate salts were not prepared by oxidation of selenocyanates with bromine, since by this method they were contaminated with triselenocyanate salts. They were, instead, obtained pure by reaction of selenium diselenocyanate with cyanide ion, and crystallization at room temperature, as discussed later.

Equilibrium (6) may also be operative under oxidation process (4), cyanide ion being captured by bromine. The reaction:



is demonstrated in this work. The reverse process, or (6) followed by



may correspondingly be operative under oxidation process (5), leading to selenium diselenocyanate.

The equilibria (6), (7), and (8) are discussed further, below, in connection with the various modes of nucleophilic attack of cyanide ion and selenocyanate ion on selenium diselenocyanate.

An improved method for the preparation of selenium diselenocyanate was worked out based on reaction (5), using bromine dissolved in benzene. As described in the experimental part, a yield of about 80 % of pure product was obtained. During the oxidation process, the formation of brown $\text{K}(\text{SeCN})_3 \cdot \frac{1}{2} \text{H}_2\text{O}$ and then the more reddish $\text{KSe}(\text{SeCN})_3 \cdot \frac{1}{2} \text{H}_2\text{O}$ is observed. Finally, the colour of the precipitate changes to the yellow of selenium diselenocyanate.

Verneuil^{3,4} prepared selenium diselenocyanate by oxidizing alkali selenocyanates with chlorine or bromine. Muthmann and Schröder⁹ reported poor yields by this method. They prepared it by treating a suspension of potassium selenocyanate in ice-cold water with dinitrogen tetroxide, and added some fuming nitric acid during the process. It has also been prepared from diselenium dibromide and silver cyanide,¹⁰ from silver selenocyanate and iodine,¹¹ by heating arenesulphenyl selenocyanates,¹² and by treating potassium selenocyanate with an excess of solid iodine pentafluoride in a sealed evacuated system below room temperature. In some of the above methods, selenocyanogen is probably formed first, and rearranges to selenium diselenocyanate and selenium dicyanide, which occurs as a side product.

REACTIONS OF SELENIUM DISELENOCYANATE WITH CYANIDE ION AND SELENOCYANATE ION

As indicated above, selenium diselenocyanate was found to react with aqueous cyanide ion, to give salts of the triselenocyanate ion and salts of the seleniumtriselenocyanate ion.

The two products crystallized from almost identical solutions, the only difference in conditions being the temperature. Crystallization at room temperature favoured the seleniumtriselenocyanate, while crystallization at lower temperature favoured the triselenocyanate. It was sometimes difficult to obtain pure products, particularly in the case of the seleniumtriselenocyanates, since the syntheses were sensitive to small alterations in the conditions.

Aqueous solutions of potassium selenocyanate were also found to react with selenium diselenocyanate, liberating selenium, and giving potassium triselenocyanate.

The selenium diselenocyanate molecule, from the crystal structure analysis by Aksnes and Foss,¹⁴ consists of an unbranched and non-planar N-C-Se-Se-C-N chain, with a Se-Se bond length of 2.33 Å, a Se-Se-Se bond angle of 101°, a Se-Se-C bond angle of 95°, and a SeSeSe/SeSeC dihedral angle of 94°. In the crystals, the molecules lie across a crystallographic mirror plane, so that the molecules have the *cis* form. The *trans* form arises from the *cis* form through a rotation of about 180° about one of the Se-Se bonds. In solution, an equilibrium between the two rotational-isomeric forms will occur.

The various modes of nucleophilic attack on the divalent selenium atoms of the selenium diselenocyanate molecule, by cyanide ion, selenocyanate ion,

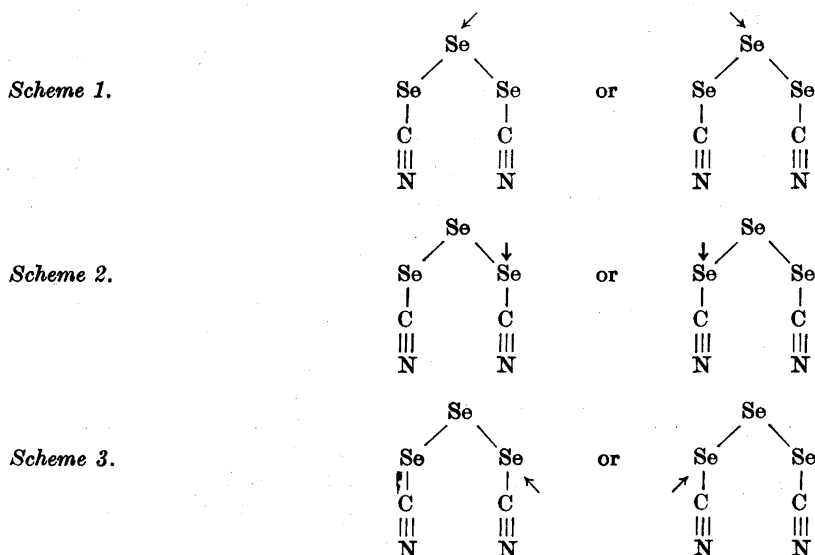
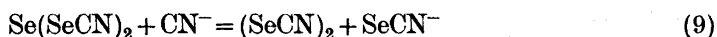


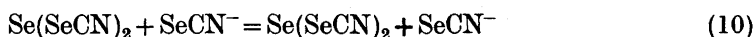
Fig. 1. Possible directions of nucleophilic attack on the divalent selenium atoms of selenium diselenocyanate, indicated by arrows.

and other nucleophiles can be envisaged as follows. An analogy is provided by the schemes for nucleophilic attack on the divalent sulphur atoms of the pentathionate ion, as discussed by Foss.²² The molecule, below, is depicted in the *cis* form, but the schemes apply equally to the *trans* form.

Scheme 1 shows an attack by the nucleophile on the middle selenium atom of selenium diselenocyanate, so as to displace (release) selenocyanate ion. With cyanide ion:



With selenocyanate ion:

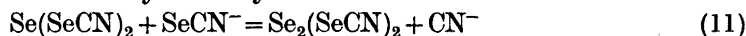


In the latter case, no change is observed, except in tracer experiments.

Attack by cyanide ion or selenocyanate ion on the middle selenium atom, and reorientation through change in bond angles and rotation about bonds, lead to stable intermediates, namely the triselenocyanate ion and selenium-triselenocyanate ion, $(\text{SeCN})_3^-$ and $\text{Se}(\text{SeCN})_3^-$, respectively. The triselenocyanate ion may subsequently, through a dissociative process, release selenocyanate ion, in which case the result will be the same as through direct displacement (9), or may release cyanide ion to reform selenium selenocyanate. The seleniumtriselenocyanate ion may release selenocyanate ion, eqn. (8), which will give the same result as direct displacement (10), or may possibly release cyanide ion to give $\text{Se} = \text{Se}(\text{SeCN})_2$. This species would be unstable and liberate selenium.

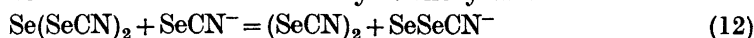
Thus, the action of cyanide ion on selenium diselenocyanate will lead to $(\text{SeCN})_3^-$, through formation of adduct or through combination of displacement products $(\text{SeCN})_2$ and SeCN^- ; to $\text{Se}(\text{SeCN})_3^-$ through combination of $\text{Se}(\text{SeCN})_2$ and displacement product SeCN^- ; to SeCN^- as displacement or dissociation product; while the reagent, CN^- , will also occur in equilibrium concentrations. Thus, all species of equilibrium (6) will be present in the reaction mixture.

Scheme 2 shows an attack on one of the terminal selenium atoms of selenium diselenocyanate, in a direction so as to displace (release) cyanide ion. In the case of attack by cyanide ion, no change will be observed, except in tracer experiments. Attack by selenocyanate ion:



will lead to a lengthening of the selenium chain of the molecule, in analogy with the building-up of sulphur chains of polythionates through displacement of sulphite by thiosulphate in presence of formaldehyde as sulphite acceptor.²³ Subsequent action of SeCN^- on $\text{Se}_2(\text{SeCN})_2$ will probably lead to liberation of selenium.

Scheme 3 shows an attack on one of the terminal selenium atoms of the molecule, the same atoms as in Scheme 2, but in a different direction, so as to release SeSeCN^- ions. In the case of attack by selenocyanate ion:



selenocyanogen will form, which with selenocyanate ion will give triselenocyanate ion, eqn. (2). The species SeSeCN^- will be unstable, and through a series of nucleophilic displacements:

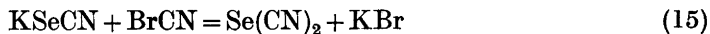


and so forth, will lead to a building-up of selenium chains and to liberation of selenium. That is, selenocyanate ion, initially through Scheme 3 displacements, will catalyze the decomposition of selenium diselenocyanate into selenocyanogen and selenium, like thiosulphate ion catalyzes the liberation of sulphur from pentathionate ion and higher polythionates.²⁴

REACTION OF SELENIUM DICYANIDE WITH SELENOCYANATE ION

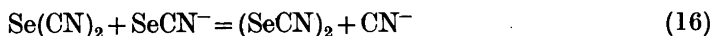
Linnemann²⁵ prepared selenium dicyanide by reacting silver selenocyanate with cyanogen iodide in ether. Verneuil⁵ prepared it by boiling selenium diselenocyanate in ether for 20 h, or by heating selenium diselenocyanate to 120°C in vacuum. It has also, as mentioned above, been obtained as a side product in some of the procedures used for the preparation of selenium diselenocyanate, where it probably is formed as a rearrangement product of selenocyanogen. The crystal structure of selenium dicyanide is known,^{26,27} and the infrared and Raman spectra have been reported.¹⁵

It was found that selenium dicyanide could be conveniently prepared by reacting potassium selenocyanate with cyanogen bromide in ether:



The reaction mixture was filtered, and on evaporation of the solution, the selenium dicyanide separated as light yellow crystals, m.p. 130–132°C. The yield was about 70 %. It may be purified through short-path vacuum sublimation, and is then colourless, m.p. 134°C.¹⁵

Selenium dicyanide was found to react with aqueous solutions of potassium selenocyanate to give potassium triselenocyanate. The first step must be an attack by selenocyanate ion on the selenium atom of selenium dicyanide, to displace (release) cyanide ion:



In presence of selenocyanate ion, selenocyanogen adds selenocyanate ion to give triselenocyanate ion, eqn. (2). A yield of about 40 % of potassium triselenocyanate, based on selenium dicyanide, eqns. (16) and (2), was obtained.

REACTIONS OF TRISELENOCYANATE ION WITH SELENOCYANATE ION AND WITH CYANIDE ION

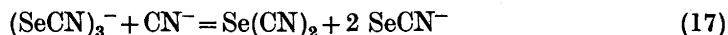
As mentioned earlier, eqn. (6), potassium triselenocyanate was found to react with potassium selenocyanate to give potassium seleniumtriselenocyanate, and cyanide. From a solution of potassium triselenocyanate in concentrated aqueous potassium selenocyanate, both potassium triselenocyanate and potassium seleniumtriselenocyanate crystallized, mostly the latter.

From crystal structure analyses,^{1,2} the triselenocyanate ion has a linear three-selenium sequence, with Se–Se bonds of about 2.66 Å, which is about

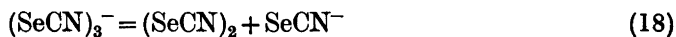
0.32 Å longer than single covalent selenium-selenium bonds. Each of the selenocyanate groups are linear, and the angle between each of the groups and the three-selenium sequence is close to 90°.

The reaction, eqn. (6), probably involves an attack by selenocyanate ion on the middle selenium atom of the triselenocyanate ion, to displace the cyanide bonded to this selenium atom.

Potassium triselenocyanate was found to react, not only with potassium selenocyanate, but also with potassium cyanide, to give selenium dicyanide and potassium selenocyanate:



The reaction, eqn. (17), can be looked upon as an attack by cyanide ion on one of the terminal selenium atoms of the triselenocyanate ion, in a direction co-linear with the three-selenium sequence, so as to release two selenocyanate ions. Also, through the dissociation equilibrium:



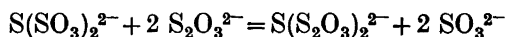
an attack on selenocyanogen may take place:



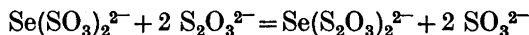
Eqns. (18) and (19) are the reverse of eqns. (2) and (16), respectively.

RELATIVE NUCLEOPHILICITIES OF CYANIDE ION AND SELENOCYANATE ION TOWARD DIVALENT SELENIUM

Inferring from the greater nucleophilicity toward divalent sulphur of cyanide ion as compared with thiocyanate ion, cyanide ion would be a better nucleophile than selenocyanate ion toward divalent selenium, although the difference would be less pronounced than in the cyanide-thiocyanate-sulphur case, due to the greater size of selenium. Toward divalent selenium, the difference in nucleophilicities of cyanide ion and even thiocyanate ion would be smaller than toward divalent sulphur (*cf.* sulphite-thiosulphate toward divalent sulphur and toward divalent selenium). The equilibrium:



lies to the left, whereas with divalent selenium as electrophile:



the equilibrium lies more to the right.²⁸

From the reactions and equilibria demonstrated in this work, eqns. (6), (9), (16), (17), (19), where selenocyanate displaces cyanide or cyanide displaces selenocyanate, depending on conditions and amounts of reagents present, the nucleophilicities of the two ions toward divalent selenium would appear to be about equal. Still, one would be inclined to believe that cyanide ion is the better nucleophile, judging from the facile reaction of cyanide ion with elemental selenium, to give selenocyanate ion.

Selenocyanate would, correspondingly, be a better leaving group than cyanide. Returning to the schemes, discussed earlier, for nucleophilic attack

on the divalent selenium atoms of selenium diselenocyanate, and comparing the SeCN^- and SeSeCN^- ions in this respect, the latter should be the better nucleophile and the former the better leaving group, judging from the expected higher acid strength of HSeCN relative to HSeSeCN . Of the leaving groups involved in the displacement of Schemes (1), (2), and (3), selenocyanate is thus indicated to be the better leaving group, so as to favour displacements according to Scheme (1).

However, the differences in nucleophilicities and in leaving group properties may not be great, and a species, present only in minute equilibrium concentrations, may undergo subsequent changes, which will completely disrupt the equilibrium and determine the course of the change.

EXPERIMENTAL

Preparation of selenocyanates

Potassium selenocyanate, KSeCN , was prepared as described in *Inorganic Syntheses*²⁹ by melting together Se and KCN. The procedure was followed, except that the melt was not allowed to solidify before it was poured into acetone.

Tetramethylammonium selenocyanate, $(\text{CH}_3)_4\text{NSeCN}$. 10 g of $(\text{CH}_3)_4\text{NCl}$ was dissolved in 40 ml methanol, and an equivalent amount of KSeCN , 13.15 g, was dissolved in 40 ml methanol. The two solutions were heated and poured together under good stirring. The solution was filtered while warm, concentrated on a water bath to 30 ml, and then stored in a refrigerator for some hours. The crystals which had deposited were filtered off, washed with a little acetone, and dried in vacuum. Yield, 11.1 g. By evaporation of the mother liquor, an additional 3.5 g were isolated. The total yield was 89 %. The salt forms non-deliquescent colourless prisms extended along the monoclinic a axis. It is soluble in and can be recrystallized from water, ethanol and acetone, or crystallized from solutions in methanol, ethanol, and acetone by addition of ether. It is not soluble in ether or chloroform.

Tetramethylammonium selenocyanate has formerly been prepared from methyl selenocyanate and trimethylamine.³⁰

Cesium selenocyanate, CsSeCN . 0.05 mol (7.20 g) of KSeCN and 0.05 mol (8.42 g) of CsCl in 50 ml acetone was heated with reflux under good stirring for 2 h. The precipitate was filtered off, washed with 50 ml warm acetone, dried, and extracted with 150 ml of methanol. After filtering, the salt was isolated by evaporation of the solution. Yield, 11.9 g, or 87 %. The salt forms non-deliquescent, colourless, orthorhombic prisms extended along the b axis. It is soluble in and can be recrystallized from water, and from methanol. It is sparingly soluble in ethanol and in acetone, not soluble in ether or chloroform. The salt can be precipitated from a solution in methanol by addition of ether. M.p. 228°C.

Cesium selenocyanate has earlier been prepared by Birkenbach and Kellermann.⁷

Preparation of triselenocyanates

Potassium triselenocyanate hemihydrate, $\text{K}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$.

a. A solution of 0.08 mol (11.52 g) of KSeCN in 15 ml water was prepared, and after addition of 30 ml benzene, the solution was chilled by placing the vessel in ice-water. 72 ml of a 0.5 M solution of bromine in benzene was slowly added under good stirring. A reddish brown, finely crystallized precipitate soon formed in the aqueous layer. The precipitate was filtered off, washed with benzene and dried in vacuum. Yield, 6.90 g, or 85 %, calculated from the amount of bromine employed. The compound was recrystallized from the mother liquor by heating to about 60°C, filtering, and leaving the filtrate in a refrigerator for 24 h. The salt forms brown prisms extended along the monoclinic b axis. (Found: Se 65.07. Calc. for $\text{K}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$: Se 65.25.)

b. 0.014 mol (0.91 g) of KCN was dissolved in 40 ml water. 0.0067 mol (1.95 g) of $\text{Se}(\text{SeCN})_2$ was added at once under vigorous stirring. The temperature was thereafter slowly raised to 40°C under continued stirring. The resulting orange solution was filtered and stored in a refrigerator for 24 h. The crystals which had formed were filtered off, washed with benzene, and dried. Yield, 0.75 g, or 31 % based on $\text{Se}(\text{SeCN})_2$, eqn. (7). (Found: Se 65.14. Calc. for $\text{K}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$: Se 65.25.)

c. 0.006 mol (0.865 g) of KSeCN was dissolved in 20 ml water, and 0.0023 mol (0.667 g) of $\text{Se}(\text{SeCN})_2$ was added at once under vigorous stirring. Selenium was liberated. The temperature was slowly raised to 45°C under continued stirring. The solution was then filtered and stored in a refrigerator for 24 h. The crystals which had deposited were filtered off, washed with benzene, and dried. Yield, 0.30 g of $\text{K}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, or 36 % based on $\text{Se}(\text{SeCN})_2$, eqns. (12) and (2). The compound was identified by X-ray method.

Rubidium triselenocyanate hemihydrate, $\text{Rb}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, was prepared from $\text{Se}(\text{SeCN})_2$ and alkali cyanide, as described for the potassium salt under b. Yield of rubidium salt, from 1.95 g $\text{Se}(\text{SeCN})_2$, 0.73 g NaCN, and 1.2 g RbCl: 1.05 g, or 38 % based on $\text{Se}(\text{SeCN})_2$, eqn. (7). (Found: Se 57.58. Calc. for $\text{Rb}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$: Se 57.85.)

The salt forms brown orthorhombic prisms extended along the *b* axis.

Cesium triselenocyanate, $\text{Cs}(\text{SeCN})_3$, was prepared in the same way as the rubidium salt, using 1.95 g $\text{Se}(\text{SeCN})_2$, 0.73 g NaCN, and 1.5 g CsCl. Yield, 1.20 g, or 40 % based on $\text{Se}(\text{SeCN})_2$, eqn. (7). (Found: Se 52.77. Calc. for $\text{Cs}(\text{SeCN})_3$: Se 52.89.)

The salt was also prepared from aqueous cesium selenocyanate by oxidation with bromine in benzene, as described for the potassium salt under a. Yield, 42 %. (Found: Se 52.33.) The products from the two methods gave identical X-ray photographs.

The salt forms brown monoclinic prisms extended along the *c* axis.

Tetramethylammonium triselenocyanate, $(\text{CH}_3)_4\text{N}(\text{SeCN})_3$, was prepared as described for the potassium salt under a. A mixture of 0.04 mol (5.76 g) of KSeCN and 0.02 mol (3.54 g) of $(\text{CH}_3)_4\text{NSeCN}$ in 75 ml water was prepared, and after addition of 50 ml benzene, 20 ml of a 1.0 M solution of bromine in benzene was slowly added under good stirring. The temperature was thereafter slowly raised to 40°C under continued stirring. The solution was then filtered, and stored in a refrigerator. Yield, 2.30 g, or 30 % based on the amount of bromine employed. (Found: Se 60.18. Calc. for $(\text{CH}_3)_4\text{N}(\text{SeCN})_3$: Se 60.88.)

A mixture of KSeCN and $(\text{CH}_3)_4\text{NSeCN}$ was used due to the low solubility, under the conditions employed, of $(\text{CH}_3)_4\text{N}(\text{SeCN})_3$.

The salt crystallized as brown orthorhombic prisms extended along the *c* axis.

Preparation of seleniumtriselenocyanates

Potassium seleniumtriselenocyanate hemihydrate, $\text{KSe}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$. 0.013 mol (0.85 g) of KCN was dissolved in 40 ml water, and 0.0062 mol (1.80 g) of $\text{Se}(\text{SeCN})_2$ was added at once under vigorous stirring. The temperature was slowly raised to 40°C under continued stirring, and small amounts of undissolved $\text{Se}(\text{SeCN})_2$ were removed by filtration. After the filtered solution had been left for about 3 h at room temperature, small amounts of $\text{Se}(\text{SeCN})_2$ had crystallized. The solution was filtered once more and set aside, at room temperature, for 24 h. The reddish brown crystals, which had deposited, were filtered off, washed with benzene, and dried. Yield, 0.50 g. (Found: Se 71.43. Calc. for $\text{KSe}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$: Se 71.45.)

Rubidium seleniumtriselenocyanate hemihydrate, $\text{RbSe}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, was prepared in the same way as the potassium salt, using 0.73 g NaCN and 1.09 g RbCl in 50 ml water, and 2.0 g $\text{Se}(\text{SeCN})_2$. During the first 3 h, a mixture of $\text{RbSe}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, $\text{Rb}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, and $\text{Se}(\text{SeCN})_2$ crystallized, and was filtered off. Afterwards, only $\text{RbSe}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ crystallized. Yield, 0.50 g. (Found: Se 64.39. Calc. for $\text{RbSe}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$: Se 64.66.)

Cesium seleniumtriselenocyanate hemihydrate, $\text{CsSe}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, was prepared in the same way as the potassium and rubidium salts, using 0.625 g NaCN and 1.01 g CsCl in 40 ml water, and 1.55 g $\text{Se}(\text{SeCN})_2$. Yield, 0.32 g. (Found: Se 59.14. Calc. for $\text{CsSe}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$: Se 58.94.)

The crystals of the potassium, rubidium, and cesium salts are triclinic, and isomorphous. They form reddish brown prisms which for the potassium and cesium salts were extended along the short *ac* diagonal, and for the rubidium salt along the *c* axis.

Preparation of selenium diselenocyanate

A solution of 0.10 mol (14.4 g) of KSeCN in 8 ml water was prepared, and after addition of 50 ml benzene, 66 ml of a 1.0 M solution of bromine in benzene was added slowly under good stirring. A reddish brown, finely crystallized precipitate first formed. At the end of the oxidation, the precipitate turned yellow. The mixture was heated under stirring, to the boiling point of benzene, and the benzene layer was decanted off. The heating and decantation procedure was repeated with 100 ml of benzene. The combined benzene solutions were stored in a refrigerator for 24 h. The crystals were filtered off, washed with cold benzene, and dried in vacuum. Yield, 7.5 g, or 78 % based on eqn. (5). (Found: Se 81.58. Calc. for $\text{Se}(\text{SeCN})_2$: 81.99.)

The infrared spectrum of the compound in Nujol, recorded, as also elsewhere in this work, on a Unicam SP 100 instrument, showed a band at 2141 cm^{-1} . This band, in Nujol, has earlier been reported at 2131 cm^{-1} .¹⁵

Preparation of selenium dicyanide

0.034 mol (3.60 g) of BrCN was dissolved in 25 ml ether, and 0.029 mol (4.20 g) of KSeCN was added at once under vigorous stirring. The temperature was raised to the boiling point of ether under continued stirring. The mixture was then filtered, and the precipitate washed with warm ether. The combined ether solutions were evaporated, and the crystallized light yellow compound was dried in vacuum, whereby also excess of BrCN was removed. Yield, 2.80 g, or 73 % based on the amount KSeCN employed. (Found: Se 60.55. Calc. for $\text{Se}(\text{CN})_2$: Se 60.28.) M.p. $130-132^\circ\text{C}$.

The infrared spectrum of the compound in Nujol showed bands at 2190 and 2182 cm^{-1} . Earlier, for selenium dicyanide in KBr or Nujol, only one band in this region, at 2171 cm^{-1} , has been reported; in acetonitrile solution, the band was resolved and found at 2183 and 2175 cm^{-1} .¹⁵

Reaction of selenium dicyanide with potassium selenocyanate

0.02 mol (2.88 g) of KSeCN was dissolved in 6 ml water, and 0.01 mol (1.31 g) of $\text{Se}(\text{CN})_2$ was added. The selenium dicyanide rapidly dissolved, and the colour of the solution turned to red orange. The solution was kept in a closed tube. After a few minutes, the crystallization of potassium triselenocyanate started. The tube was placed in a refrigerator and kept there for 24 h. The crystals were then filtered off, washed with benzene, and dried. Yield, 1.85 g of $\text{K}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, or 42 % based on $\text{Se}(\text{CN})_2$, eqns. (16) and (2).

Reactions of potassium triselenocyanate with potassium selenocyanate and with potassium cyanide

With potassium selenocyanate. 0.06 mol (0.86 g) of KSeCN was dissolved in 0.4 ml water, and 0.0072 mol (0.26 g) of $\text{K}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ was added. The potassium triselenocyanate dissolved in the selenocyanate solution on heating to about 60°C . The warm, red orange solution was left at room temperature. A mixture of $\text{KSe}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ and $\text{K}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ crystallized, mostly the former.

With potassium cyanide. 0.0033 mol (0.215 g) of KCN was dissolved in 1.5 ml water, and 0.003 mol (1.09 g) of $\text{K}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ was added at once under stirring. The potassium triselenocyanate dissolved in the cyanide solution, and the colour of the solution turned to yellow. 25 ml ether was added to the solution, and the stirring continued. The ether layer turned yellow, and was decanted off. This extraction and decantation procedure was repeated twice, with 25 ml of ether each time. The combined ether solutions were evaporated to dryness, and the residue was dissolved in 10 ml ether. The solution was filtered and evaporated to dryness. Yellow crystals of $\text{Se}(\text{CN})_2$ remained. Yield, 0.210 g, or 53 % based on eqn. (17). The compound was identified through its infrared spectrum.

Table 1. Space groups and cell dimensions for alkali salts and tetramethylammonium salt of the triselenocyanate ion. The *F*-centered setting for the potassium salt has been chosen in order to bring out the analogy with the crystals of the rubidium salt. In the conventional *C*2 setting, *c* = 13.834 Å, β = 121.95°, with four formula units per unit cell.

Salt	Space group	Formula units per unit cell	Axial lengths (Å)			β	Density	
			<i>a</i>	<i>b</i>	<i>c</i>		Found	Calc.
K(SeCN) ₃ ·½H ₂ O	<i>F</i> 2 (No. 5)	8	16.988(8)	4.443(3)	23.590(10)	95.70(5)°	2.74	2.72
Rb(SeCN) ₃ ·½H ₂ O	<i>Fm</i> 2 <i>m</i> (No. 42)	8	16.710(8)	4.833(3)	22.808(10)		2.96	2.95
Cs(SeCN) ₃	<i>C</i> c (No. 9) or <i>C</i> 2/ <i>c</i> (No. 15)	4	7.969(4)	21.156(10)	5.593(4)	96.84(6)°	3.18	3.18
(CH ₃) ₄ N(SeCN) ₃	<i>Pn</i> 2 ₁ <i>a</i> (No. 33) or <i>Fnma</i> (No. 62)	4	8.06(4)	18.55(10)	9.06(5)		1.91	1.91

Table 2. Cell dimensions for alkali salts of the seleniumtriselenocyanate ion. The salts are triclinic with four formula units per unit cell.

Salt	Axial lengths (Å)			β	γ	Density		
	<i>a</i>	<i>b</i>	<i>c</i>			Found	Calc.	
KSe(SeCN) ₃ ·½H ₂ O	9.170(2)	13.377(3)	9.057(2)	106.22(2)°	100.64(2)°	99.07(2)°	2.89	2.87
RbSe(SeCN) ₃ ·½H ₂ O	9.144(2)	13.227(3)	9.180(2)	105.03(2)°	100.02(2)°	96.11(2)°	3.12	3.11
CsSe(SeCN) ₃ ·½H ₂ O	9.242(5)	13.533(6)	9.245(5)	104.90(5)°	99.79(5)°	99.89(5)°	3.29	3.27

CRYSTAL DATA

Unit cell dimensions for salts of the triselenocyanate ion are given in Table 1, and for salts of the seleniumtriselenocyanate ion in Table 2. The unit cell dimensions were determined from zero-layer Weissenberg photographs, except for $\text{KSe}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ and $\text{RbSe}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, where measurements were carried out on a Siemens AED diffractometer. Photographs taken around the three axes were used for $\text{Cs}(\text{SeCN})_3$ and $\text{CsSe}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, around the a and b axes for $\text{K}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, and around the b and c axes for $\text{Rb}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$.

The measurements, from 30 to 75 observations for each salt, were evaluated by means of a least squares program, except for $(\text{CH}_3)_4\text{N}(\text{SeCN})_3$, where only axial reflections were used.

Cell dimensions for cesium selenocyanate and tetramethylammonium selenocyanate were determined from axial reflections on zero-layer Weissenberg photographs taken around the three axes. Estimated standard deviations are given in parentheses.

Cesium selenocyanate, CsSeCN , forms orthorhombic prisms extended along the b axis, with $a = 8.17(4)$ Å, $b = 6.42(3)$ Å, and $c = 8.55(4)$ Å. There are four formula units per unit cell; density, calc. 3.52, found 3.53 g/cm³. The space group is $Pn2_1a$ (No. 33) or $Pnma$ (No. 62).

Tetramethylammonium selenocyanate, $(\text{CH}_3)_4\text{NSeCN}$, forms monoclinic prisms extended along the a axis, with $a = 7.76(4)$ Å, $b = 8.82(4)$ Å, $c = 12.12(6)$ Å, and $\beta = 87.6(3)^\circ$. There are four formula units per unit cell; density, calc. 1.43, found 1.42 g/cm³. The space group is $P2_1/c$ (No. 14).

$\text{CuK}\alpha$ radiation was used for the Weissenberg photographs, $\lambda(\alpha_1) = 1.5405$ Å, $\lambda(\alpha_2) = 1.5443$ Å, or $\lambda = 1.5418$ Å for unresolved α_1 and α_2 reflections. Diffractometer data were recorded with $\text{MoK}\alpha$ radiation, $\lambda(\alpha_1) = 0.70926$ Å; only resolved reflections were used for determination of cell dimensions.

The space groups, for all compounds, were found from systematic absences, and for $\text{K}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ and $\text{Rb}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ by subsequent structure analyses.

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