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The Crystal Structure of Potassium Seleniumtriselenocyanate Hemihydrate

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The crystal structure of potassium seleniumtriselenocyanate hemihydrate, $KSe(SeCN)_3 \cdot \frac{1}{2} H_2O$, has been determined by X-ray methods, and refined by full matrix least squares procedures. The crystals are triclinic, space group $P\bar{1}$ (No. 2), with $a = 9.170(2)$ Å, $b = 13.377(3)$ Å, $c = 9.057(2)$ Å, $\alpha = 106.22(2)°$, $\beta = 100.64(2)°$, $\gamma = 99.07(2)°$, and four formula units per unit cell.

In the crystals, the seleniumtriselenocyanate ions are dimerized. The eight selenium atoms of the dimerized unit are approximately coplanar, and the six cyano groups are located on the same side of the plane. The Se – Se – Se bond angles are in the ranges from 170.58(6) to 174.94(5)° and from 86.13(5) to 98.41(5)°. There are four rather short Se – Se bonds, from 2.395(2) to 2.419(2) Å, and four long ones, from 3.089(2) to 3.255(2) Å. The short ones are significantly longer than the Se – Se single-bond distance, 2.34 Å, and the long ones are shorter than van der Waals approaches. Each long Se – Se bond occurs *trans* to a short Se – Se bond. The total lengths of the rather unsymmetrical, approximately linear three-selenium systems (the sum of the lengths of the two Se – Se bonds) are from 5.508 to 5.647 Å. This is 0.19 to 0.33 Å longer than the total lengths of the more symmetrical linear three-selenium systems of the triselenocyanate ion.

The dimerized unit can be looked upon as built up of two selenium diselenocyanate molecules, $Se(SeCN)_2$, bridged together through the selenium atoms of two selenocyanate ions.

Several rather short Se···Se contacts, from 3.34 Å upwards, occur between eight-selenium units.

In 1884 – 1886 Verneuil [1] isolated and determined the composition of potassium seleniumtriselenocyanate, $KSe(SeCN)_3 \cdot \frac{1}{2} H_2O$, although he described it as a monohydrate. Its crystal structure analysis, reported here, has been carried out as a part of a study of linear three-selenium systems.

CRYSTAL DATA

Preparative and crystallographic data on potassium seleniumtriselenocyanate hemihydrate and other seleniumtriselenocyanates have been reported earlier.[2] A short note on the crystal structure of the potassium salt has also been reported.[3]

The salt, $KSe(SeCN)_3 \cdot \frac{1}{2} H_2O$, forms reddish-brown prisms extended along the short *ac* diagonal, with $a = 9.170(2)$ Å, $b = 13.377(3)$ Å, $c = 9.057(2)$ Å, $\alpha = 106.22(2)°$, $\beta = 100.64(2)°$, and $\gamma = 99.07(2)°$. Collection of X-ray data was done by means of a Siemens AED diffractometer, using Nb-filtered Mo$K\alpha$ radiation, $\lambda(\alpha_1) = 0.70926$ Å. For determination of cell parameters, θ, ϕ, and X settings for 23 reflections with high θ-values were measures and evaluated by means of a least squares program.

There are four formula units per unit cell; density, calc. 2.87, found 2.89 g/cm^3. The space group, from structure analysis is $P\bar{1}$ (No. 2).

The crystal used for data collection had the following dimensions, given as distances to faces from the point of intersections of the crystal faces $(0\bar{1}0)$, $(\bar{1}01)$, and (101): to (010), 0.114 mm; to $(10\bar{1})$, 0.158 mm; to $(\bar{1}0\bar{1})$, 0.336 mm.

Intensity data were collected using a "five value" measuring procedure. The net count of two reference reflections measured at intervals of 50 reflections, fell by about 14 % during the collection period. The lower limit for observed reflections was set equal to three times the standard deviation in net intensity. 3150 out of 4945 reflections with $\theta < 28°$ were found to be stronger than the lower limit. The remaining reflections were judged as unobserved and set equal to the limit. 24 reflections which showed extraordinary high, or erratic, background count were at a later stage omitted from the data.

The intensities were corrected for absorption.[4] The linear absorption coefficient, $\mu = 159.4$ cm^{-1}.

Table 1. Atomic coordinates for potassium selenium triselenocyanate in fractions of triclinic cell edges. Origin at a centre of symmetry. Standard deviations from least squares are given in parentheses.

	x	y	z
Se_1	0.06300(10)	0.13858(7)	−0.06314(10)
Se_2	0.07100(9)	0.12554(7)	0.19737(10)
Se_3	−0.19849(10)	0.10495(8)	0.18396(12)
Se_4	0.72016(9)	0.12574(7)	0.60281(10)
Se_5	0.46001(9)	0.13382(7)	0.60678(9)
Se_6	0.47137(10)	0.13623(8)	0.87409(10)
Se_7	0.41279(11)	0.12399(7)	0.24275(10)
Se_8	0.11004(10)	0.13602(8)	0.56510(11)
C_1	0.1420(10)	0.2862(8)	−0.0010(10)
C_2	−0.1851(10)	0.2454(9)	0.2837(12)
C_4	0.7986(9)	0.2666(8)	0.7337(10)
C_6	0.5298(10)	0.2824(8)	0.9653(10)
C_7	0.4534(9)	0.2685(8)	0.3346(10)
C_8	0.1771(10)	0.2785(8)	0.6131(10)
N_1	0.1809(10)	0.3745(7)	0.0265(10)
N_3	−0.1767(11)	0.3339(8)	0.3434(14)
N_4	0.8458(9)	0.3514(6)	0.8199(10)
N_6	0.5699(11)	0.3725(7)	0.0220(10)
N_7	0.4751(10)	0.3575(7)	0.3941(10)
N_8	0.2201(10)	0.3685(7)	0.6432(10)
O	0.1767(8)	0.4831(6)	0.3874(8)
K_1	0.5560(3)	0.4726(2)	0.7336(3)
K_2	0.9099(3)	0.4773(2)	0.1697(3)

Table 2. Anistropic thermal parameters (Å²) in the form $\exp[-2\pi^2(h^2a^{-2}U_{11}+\cdots+2hka^{-1}b^{-1}U_{12}\cdots)]$. All values have been multiplied by 10^3. Standard deviations from least squares refinement in parentheses.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Se_1	35.0(5)	29.4(5)	24.8(4)	4.0(4)	9.9(3)	5.0(4)
Se_2	27.9(4)	29.6(4)	25.0(4)	3.7(3)	9.2(3)	5.4(3)
Se_3	35.4(5)	35.8(5)	36.0(5)	3.4(4)	13.4(4)	7.2(4)
Se_4	30.0(5)	44.7(6)	44.2(5)	3.5(4)	9.0(4)	7.9(4)
Se_5	34.2(5)	32.6(5)	34.0(5)	7.7(4)	7.6(4)	4.0(4)
Se_6	26.7(4)	23.8(4)	23.9(4)	5.0(3)	6.5(3)	4.5(3)
Se_7	42.1(5)	35.9(5)	26.0(4)	5.6(4)	11.2(4)	7.6(4)
Se_8	25.3(4)	31.1(5)	33.5(4)	5.9(3)	4.4(3)	5.1(3)
C_1	40(5)	29(5)	33(4)	−2(4)	10(4)	4(4)
C_2	38(5)	35(5)	31(4)	8(4)	8(4)	16(4)
C_4	31(5)	44(6)	61(6)	8(4)	25(5)	18(4)
C_6	30(4)	36(5)	25(4)	8(4)	14(4)	8(3)
C_7	41(5)	42(6)	24(4)	7(4)	7(4)	8(4)
C_8	23(4)	40(6)	38(5)	5(4)	18(4)	1(4)
N_1	74(5)	42(5)	40(4)	−7(4)	12(4)	6(4)
N_3	81(6)	42(5)	50(5)	21(5)	17(4)	27(5)
N_4	68(6)	46(6)	120(9)	17(5)	24(6)	17(5)
N_6	64(6)	37(5)	54(5)	8(4)	11(4)	17(4)
N_7	93(7)	40(6)	43(5)	0(5)	1(4)	24(5)
N_8	38(4)	29(4)	57(5)	0(3)	5(4)	1(4)
O	58(4)	53(4)	52(4)	6(3)	22(3)	9(3)
K_1	47.8(12)	37.6(12)	38.9(11)	4.6(10)	10.2(9)	6.2(9)
K_2	44.6(11)	36.8(12)	43.2(11)	3.5(9)	9.4(9)	11.7(9)

THE STRUCTURE ANALYSIS

The structure was solved by Patterson and Fourier methods and refined to an R-value of 0.042. The three-dimensional Fourier difference map based on the data of the final refinement showed no peak higher than 0.9 e Å^{-3}.

Computational procedures and programs used are described elsewhere.[5]

The final atomic coordinates and temperature parameters are listed in Tables 1 and 2.

The structure factors are available from the author on request.

RESULTS

The di-μ-selenocyanato-bis{diselenocyanatoselenate(II)} anion. Bond lengths, close contacts, and angles in the anion, based on the atomic coordinates of Table 1, are given in Fig. 1 and Tables 3 and 4. Distances from the potassium ions and from the water molecule to neighbouring atoms are given in Table 5. The uncertainties in cell dimensions are taken into account in the given standard deviations. In the tables, superscript I denotes an atom at $(x,y,z-1)$, II at $(1+x,y,z)$, III at $(x-1,y,z)$, IV at $(x,y,1+z)$, V at $(\bar{x},\bar{y},\bar{z})$, VI at $(1-x,\bar{y},1-z)$, VII at $(\bar{x},\bar{y},1-z)$, VIII at $(1-x,1-y,1-z)$, IX at $(1-x,1-y,\bar{z})$, X at $(2-x,1-y,1-z)$, and XI at $(\bar{x},1-y,1-z)$, where x, y, z are the coordinates of Table 1.

In the crystal structure of potassium seleniumtriselenocyanate, layers of selenium atoms occur parallel to the *ac* plane at y approximately 0.128 and −0.128. The selenium atoms of a layer are held together through bonds and through weaker interactions. Two layers, interrelated through symmetry centres at $y=0$, are held together through short Se···Se contacts, making a double layer. The cyano groups are located on the outsides of the double layer, and the potassium ions and the water molecules are located between the double layers.

As seen from Fig. 1, the seleniumtriselenocyanate ions are dimerized in the crystals. The eight selenium atoms of the dimerized unit, *i.e.* the two central atoms, Se_2 and Se_5, the four terminal atoms, Se_1, Se_3, Se_4, and Se_6, and the two bridging atoms, Se_7 and Se_8, are approximately co-planar. The largest deviation of an atom from a least squares plane is −0.21 Å.

Each of the two central selenium atoms, Se_2 and Se_5, has a distorted square-planar environment, with long bonds to bridging selenium atoms *trans* to rather short bonds to terminal selenium atoms. The variation in the lengths of the short Se−Se bonds, from 2.395(2) to 2.419(2) Å, is small, but significant. The short bonds are definitely longer than the Se−Se single bond distance, 2.34 Å. The long bonds are from 3.092(2) to 3.244(2) Å, and thus shorter than van der Waals approaches. The Se−Se−Se angles of the four approximately linear three-selenium systems at each central selenium atoms are from 170.58 to 174.94°. The total lengths of these rather unsymmetrical systems (the sum of the lengths of the two Se−Se bonds) are 5.508 to 5.647 Å, and thus 0.19 to 0.33 Å longer than the more symmetrical linear three-selenium systems of the triselenocyanate ion.[6-8]

Approximately in the plane of the eight-selenium unit, each terminal selenium atom has a close contact to a bridging selenium atom of a neighbouring eight-selenium unit, and each bridging selenium atom has two close contacts to terminal selenium atoms of two neighbouring eight-selenium units (*cf.* Fig. 1). The contacts are from 3.464 Å and upwards. The Se−Se···Se angles are from 164.11 to 172.58°. Each of the linear three-selenium system thereby has short contacts in both ends, of equal length. These short contacts have probably some influence on the bond

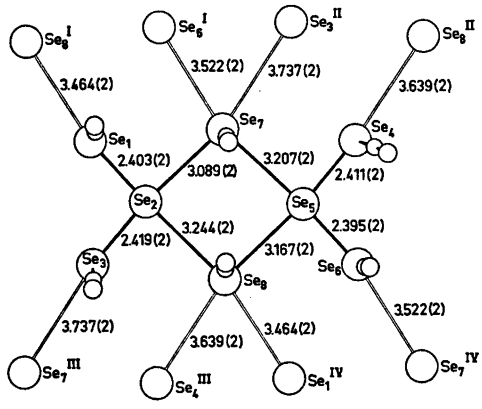

Fig. 1. The di-μ-selenocyanato-bis{diselenocyanatoselenate(II)} anion in $KSe(SeCN)_3 \cdot \frac{1}{2} H_2O$, as seen normal to the *ac* plane.

Table 3. Angles (°) in the plane of the eight selenium unit. Standard deviations in parentheses.

$Se_1-Se_2-Se_3$	97.60(5)	$Se_4-Se_5-Se_6$	98.41(5)
$Se_3-Se_2-Se_8$	86.13(5)	$Se_6-Se_5-Se_8$	88.54(5)
$Se_8-Se_2-Se_7$	87.32(5)	$Se_8-Se_5-Se_7$	86.64(4)
$Se_7-Se_2-Se_1$	89.64(5)	$Se_7-Se_5-Se_4$	83.37(5)
$Se_1-Se_2-Se_8$	173.06(5)	$Se_4-Se_5-Se_8$	172.81(5)
$Se_3-Se_2-Se_7$	170.58(6)	$Se_6-Se_5-Se_7$	174.94(5)
$Se_2-Se_1\cdots Se_6^{I}$	169.29(5)	$Se_2-Se_7\cdots Se_3^{II}$	165.17(4)
$Se_2-Se_3\cdots Se_7^{III}$	167.62(4)	$Se_5-Se_7\cdots Se_6^{I}$	164.11(4)
$Se_5-Se_4\cdots Se_8^{II}$	172.58(5)	$Se_2-Se_8\cdots Se_1^{IV}$	167.03(4)
$Se_5-Se_6\cdots Se_7^{IV}$	169.17(5)	$Se_5-Se_8\cdots Se_4^{III}$	166.88(4)
$Se_5-Se_7\cdots Se_3^{II}$	100.45(4)	$Se_2-Se_8\cdots Se_4^{III}$	100.82(4)
$Se_2-Se_7\cdots Se_6^{I}$	101.03(4)	$Se_5-Se_8\cdots Se_1^{IV}$	100.90(4)
$Se_6\cdots Se_7\cdots Se_3^{II}$	64.74(4)	$Se_4^{III}\cdots Se_8\cdots Se_1^{IV}$	66.27(4)

Table 4. Bond lengths and short distances (Å) and angles (°) out of the plane of the eight selenium unit. Standard deviations in parentheses.

Se_1-C_1	1.876(10)	$\angle Se_1-C_1-N_1$	174.6(7)
C_1-N_1	1.121(13)	$\angle Se_2-Se_1-C_1$	97.2(3)
Se_3-C_3	1.817(11)	$\angle Se_3-C_3-N_3$	178.6(10)
C_3-N_3	1.139(15)	$\angle Se_2-Se_3-C_3$	94.6(3)
Se_4-C_4	1.866(9)	$\angle Se_4-C_4-C_4$	176.8(8)
C_4-N_4	1.145(11)	$\angle Se_5-Se_4-C_4$	93.9(3)
Se_6-C_6	1.843(10)	$\angle Se_6-C_6-N_6$	178.1(8)
C_6-N_6	1.139(13)	$\angle Se_5-Se_6-C_6$	96.5(3)
Se_7-C_7	1.824(10)	$\angle Se_7-C_7-N_7$	177.7(8)
C_7-N_7	1.129(13)	$\angle Se_2-Se_7-C_7$	87.9(3)
		$\angle Se_5-Se_7-C_7$	81.0(3)
Se_8-C_8	1.808(10)	$\angle Se_8-C_8-N_8$	179.7(8)
C_8-N_8	1.144(14)	$\angle Se_2-Se_8-C_8$	86.3(3)
		$\angle Se_5-Se_8-C_8$	83.8(3)
$Se_2\cdots Se_1^{V}$	3.339(2)	$\angle Se_1-Se_2\cdots Se_1^{V}$	93.47(5)
		$\angle Se_3-Se_2\cdots Se_1^{V}$	76.17(5)
		$\angle Se_7-Se_2\cdots Se_1^{V}$	97.47(4)
		$\angle Se_8-Se_2\cdots Se_1^{V}$	93.11(4)
$Se_5\cdots Se_4^{VI}$	3.426(2)	$\angle Se_4-Se_5\cdots Se_4^{VI}$	100.36(4)
		$\angle Se_6-Se_5\cdots Se_4^{VI}$	101.78(5)
		$\angle Se_7-Se_5\cdots Se_4^{VI}$	75.59(4)
		$\angle Se_8-Se_5\cdots Se_4^{VI}$	76.26(4)
$Se_1\cdots Se_2^{V}$	3.339(2)	$\angle Se_2-Se_1\cdots Se_2^{V}$	86.53(5)
		$\angle C_1-Se_1\cdots Se_2^{V}$	176.1(3)
$Se_4\cdots Se_5^{VI}$	3.426(2)	$\angle Se_5-Se_4\cdots Se_5^{VI}$	79.63(4)
		$\angle C_4-Se_4\cdots Se_5^{VI}$	172.1(3)
$Se_8\cdots Se_8^{VII}$	3.621(2)	$\angle Se_2-Se_8\cdots Se_8^{VII}$	89.22(4)
		$\angle Se_5-Se_8\cdots Se_8^{VII}$	109.18(4)
		$\angle C_8-Se_8\cdots Se_8^{VII}$	166.4(3)

Table 5. Distances from the potassium ions and from the water molecule. Bond lengths (Å) and angles (°). Standard deviations are given in parentheses.

$K_1\cdots N_7$	2.920(9)	$\angle N_7\cdots K_1\cdots N_8$	72.7(3)
$K_1\cdots N_8$	3.029(10)		
$K_1\cdots N_1^{VIII}$	2.958(8)	$\angle N_1^{VIII}\cdots K_1\cdots N_6^{VIII}$	72.3(3)
$K_1\cdots N_6^{VIII}$	3.108(11)	$\angle N_1^{VIII}\cdots K_1\cdots N_7^{VIII}$	86.0(3)
$K_1\cdots N_7^{VIII}$	2.854(11)	$\angle N_6^{VIII}\cdots K_1\cdots N_7^{VIII}$	76.3(3)
$K_1\cdots O^{VIII}$	2.909(9)		
$K_2\cdots N_6$	3.084(10)	$\angle N_6\cdots K_2\cdots N_4^{IV}$	67.2(3)
$K_2\cdots N_4^{IV}$	3.039(9)	$\angle N_6\cdots K_2\cdots N_3^{III}$	73.5(3)
$K_2\cdots N_3^{III}$	2.907(14)	$\angle N_4^{IV}\cdots K_2\cdots N_3^{III}$	109.4(3)
$K_2\cdots N_1^{IX}$	3.118(11)	$\angle N_1^{IX}\cdots K_2\cdots N_8^{VII}$	72.5(3)
$K_2\cdots N_8^{VII}$	2.849(10)	$\angle N_1^{IX}\cdots K_2\cdots N_4^{X}$	64.2(3)
$K_2\cdots N_4^{X}$	2.909(9)	$\angle N_8^{VII}\cdots K_2\cdots N_4^{X}$	89.3(3)
$K_2\cdots O^{II}$	2.820(8)		
$O\cdots N_8$	3.116(13)	$\angle N_8\cdots O\cdots N_3^{XI}$	83.6(4)
$O\cdots N_3^{XI}$	2.933(13)	$\angle N_8\cdots O\cdots K_1^{VII}$	114.4(3)
$O\cdots K_1^{VIII}$	2.909(9)	$\angle N_8\cdots O\cdots K_2^{III}$	129.7(3)
$O\cdots K_2^{III}$	2.820(8)	$\angle N_3^{XI}\cdots O\cdots K_1^{VII}$	110.0(3)
		$\angle N_3^{XI}\cdots O\cdots K_2^{III}$	100.8(3)
		$\angle K_1^{VIII}\cdots O\cdots K_2^{III}$	110.9(3)

lengths in the three-selenium system, particularly on the long bonds between central atoms and bridging atoms. Thus, the Se_2-Se_7 bond length is 3.089 Å and the $Se_7\cdots Se_3^{II}$ distance is 3.737 Å. The effect, if any, of Se_3^{II} on the Se_2-Se_7 bond length is probably small. On the other hand, the Se_2-Se_8 bond length is 3.244 Å and the close contact $Se_8\cdots Se_1^{IV}$ is 3.464 Å; the Se_5-Se_7 bond length is 3.207 Å and the contact $Se_7\cdots Se_6^{I}$ is 3.522 Å; the Se_5-Se_8 bond length is 3.167 and the contact $Se_8\cdots Se_4^{III}$ is 3.639 Å.

The close contacts may also have a small influence on the rather short Se–Se bond lengths between the central atoms and the terminal atoms. In the approximately linear

a *b* *c*

system $-Se\cdots Se-Se-Se-$, the short bond length *b* is probably to some degree influenced by the neighbouring atoms on both sides. Since the bond *b* has nearly the strength of a covalent bond and since the difference between *a* and *c* is rather small, from 0.22 Å and upwards, and a relatively short bond *c* occurs together with a relative long *a*, and *vice versa*, the total effect on *b* is expected to be small.

The six cyano groups of the eight-selenium unit are all located at the same side of the least squares plane through the unit, and the Se–C bonds makes angles of 70.3 to 82.7° with the plane. Only one of the selenocyanate groups, $Se_1-C_1-N_1$, has a significant devia-

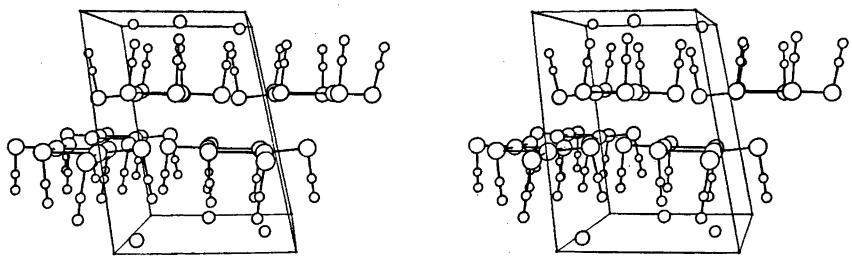

Fig. 2. A stereoscopic pair of drawings of $KSe(SeCN)_3.\frac{1}{2}H_2O$. The cell drawn is along the *a* and *c* axes from 0 to 1 and along *b* axis from $-\frac{1}{2}$ to $\frac{1}{2}$.

tion from linearity, the $Se_1-C_1-N_1$ angle being 174.6(7)°. The Se–C bond lengths are from 1.808(10) to 1.876(10) Å, with mean value 1.839 Å. As seen from Table 4, the two selenium atoms Se_1 and Se_4 with the longest Se–C bond lengths have close contacts to selenium atoms located *trans* to the carbon atoms. Thus, the Se_1-C_1 bond length is 1.876(10) Å, the $Se_1\cdots Se_2^V$ distance is 3.339(2) Å, and the angle $C_1-Se_1\cdots Se_2^V$ is 176.1(3)°. The Se_4-C_4 is 1.866(9) Å, the $Se_4\cdots Se_5^{VI}$ is 3.426(2) Å, and $C_4-Se_4\cdots Se_5^{VI}$ is 172.1(3)°. This tendency of lengthening of the Se–C bond caused by the close contact *trans* to the Se–C bond is uncertain since the standard deviations are rather large.

The C–N bond lengths, from 1.121(13) to 1.145(11) Å, are equal within the accuracy of the structure analysis.

The dimensions of the selenocyanate groups are in the same range as have been found earlier.[6–9]

The close selenium-selenium contacts from atoms in the layer at y approximately 0.128 to atoms in the layer at y approximately −0.128, occur, as mentioned above, from Se_1 to Se_3^V and from Se_4 to Se_5^{VI}. Furthermore, the central selenium atom Se_2 has a close contact to Se_1^V, the distance is 3.339 Å and the angles $Se-Se_2\cdots Se_1^V$ are from 76.17 to 97.47°. The other central selenium atom, Se_5, has a contact to Se_4^{VI}, 3.426 Å; the angles $Se-Se_5\cdots Se_4^{VI}$ are from 75.59 to 101.78°. The distance between the two bridging selenium atoms Se_8 and Se_8^{VII} is 3.621 Å and the angle $C_8-Se_8\cdots Se_8^{VII}$ is 166.4°.

The central selenium atoms, Se_2 and Se_5, have both a square-planar coordination. The tendency of selenium(II) and of tellurium(II) in their complexes toward square-planar coordination is well known.[10] It is therefore likely that the central selenium atoms, in the present structure, are acting as donors in the fifth approaches which are at approximately right angles to the square-planar coordinations.

The eight-selenium unit can be looked upon as built up of two selenium diselenocyanate molecules $Se(SeCN)_2$, bridged together through the selenium atoms of two selenocyanate ions. In the crystals of selenium diselenocyanate,[10–12] the molecules lie across a crystallographic mirror plane, with the middle selenium atom in the plane; the Se–Se bond lengths are 2.33 Å and the Se–Se–Se angle is 103°. Short Se···N contacts occur in directions which indicate a tendency to square-planar coordination at all selenium atoms. The Se···N distances at the central selenium atom are both 3.16 Å, and at each of the terminal selenium atoms, 3.07 and 3.27 Å. In the present adduct with potassium selenocyanate, the selenium diselenocyanate molecules retain their approximate shape. The Se–Se bond is now being approached at approximately 180° by a selenium atom of a selenocyanate group with the CN part of the group at right angle to the approach, instead of by the nitrogen end of a selenocyanate group. The approach is now stronger and the Se–Se bonds, *trans* to the approach, become a little longer.

The tendency to square-planar coordination at the terminal selenium atoms of selenium diselenocyanate are found in the present structure at Se_1 and Se_4. Se_1 is bonded to C_1 and to Se_2. The bond lengths are 1.876 and 2.403 Å, respectively; the $Se_2-Se_1-C_1$ angle is 97.2°. The Se_1-Se_2 bond is approached at 169.29° by Se_8^I, the $Se_1\cdots Se_8^I$ distance is 3.464 Å. The C_1-Se_1 bond is approached at 176.1° by Se_3^V, the $Se_1\cdots Se_3^V$ distance is 3.339 Å. The atoms Se_8^I and Se_3^V are 0.622 and 0.077 Å, respectively, from the plane through $Se_2Se_1C_1$. The surroundings of the terminal selenium atom Se_4, are much the same as for Se_1. Se_4 is bonded to C_4 and to Se_5. The bond lengths are 1.866 and 2.411 Å, respectively; the $Se_5-Se_4-C_4$ angle is 93.9°. The Se_4-Se_5 bond is approached at 172.59° by Se_8^{II}, the $Se_4\cdots Se_8^{II}$ distance is 3.639 Å. The C_4-Se_4 bond is approached at 172.1° by Se_5^{VI}, the $Se_4\cdots Se_5^{VI}$ distance is 3.426 Å. The atoms Se_8^{II} and Se_5^{VI} are −0.442 and 0.273 Å, respectively, out of the plane through $Se_5Se_4C_4$. The terminal selenium atoms Se_3 and Se_6 have close contacts *trans* to Se_3-Se_2 and Se_6-Se_5, respectively, but no close contacts *trans* to the cyano groups.

The environment of the potassium ions and the water molecule. The potassium ions and the water molecule lie at y approximately ½, between double layers of selenium atoms around $y=0$ and 1. The closest contacts of the potassium ions and of the water molecule are listed in Table 5. The water molecule is surrounded by two potassium ions, at distances

of 2.820 and 2.909 Å and K···O···K angle of 110.9°, and by two nitrogen atoms, at distances of 2.933 and 3.116 Å and a N···O···N angle of 83.6°. The latter contacts probably involve weak O–H···N hydrogen bonds. The arrangement around the water molecule is approximately tetrahedral, the K···O···N angles being in the range 105.3 to 129.7°.

The potassium ion K_2 is surrounded by six nitrogen atoms, at distances ranging from 2.849 to 3.118 Å, and by one oxygen atom, at 2.820 Å. The shape of the resulting polyhedron is rather irregular. Three of the nitrogen atoms lie on a plane above and three lie in a plane below the potassium ion; both planes are approximately parallel to the *ac* plane. The oxygen atom lies between the two planes.

The surroundings of the potassium ion K_1 is much the same as of K_2 with the exception that one of the nitrogen atoms below potassium is missing. The distances from K_1 to the nitrogen atoms are in the range 2.854 to 3.108 Å, and the distance from K_1 to oxygen is 2.909 Å.

The K···O distances are in the normal range (*cf.* Ref. 13, p. 258) and so are the K···N distances. The sum of the K···N ionic radii is 3.04 Å. In potassium selenocyanate,[9] the closest K···N distances are 2.89, 2.94, and 3.12 Å; in potassium thiocyanate,[14] 2.97 and 2.89 Å, and in potassium triselenocyanate hemihydrate,[7] in the range 2.86 to 3.04 Å.

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