

The Crystal Structure of Rubidium Triselenocyanate Hemihydrate

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The crystal structure of rubidium triselenocyanate hemihydrate, $\text{Rb}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, has been determined by X-ray methods, and refined by full-matrix least squares procedures. The crystals are orthorhombic, space group $Fm2m$ (No. 42), with $a = 16.710(8)$ Å, $b = 4.833(3)$ Å, $c = 22.808(10)$ Å, and eight formula units per unit cell.

In the crystals, the triselenocyanate ions lie across crystallographic mirror planes. The three-selenium sequence of the triselenocyanate ion is nearly linear, with Se-Se-Se bond angle $176.9(3)^\circ$, and Se-Se bond lengths of $2.656(3)$ Å, which is 0.32 Å longer than single covalent selenium-selenium bonds.

Each of the selenocyanate groups is linear within the error. The terminal selenocyanate groups and the middle selenium atom, Se_2 , lie nearly in the same plane. This plane makes an angle of 65.0° with a plane through the middle selenocyanate group and the terminal selenium atoms.

The triselenocyanate ion was first isolated by Verneuil¹ in the form of the potassium salt. The crystal structure of the potassium salt, a hemihydrate, has been determined.² Birckenback and Kellermann³ prepared the cesium salt. Later, rubidium triselenocyanate hemihydrate, $\text{Rb}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, was isolated.⁴ Its crystal structure analysis, reported here, has been carried out as part of a study of linear three-selenium systems.

CRYSTAL DATA

Preparative and crystallographic data on rubidium triselenocyanate hemihydrate have been reported earlier.⁴

The salt, $\text{Rb}(\text{SeCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, forms long, brown, orthorhombic prisms elongated along the b axis, with $a = 16.710(8)$ Å, $b = 4.833(3)$ Å, and $c = 22.808(10)$ Å. The unit cell dimensions were determined from zero-layer Weissenberg photographs around the b and c axes, and evaluated by means of a least squares program.

There are eight formula units per unit cell; density, calc. 2.95, found 2.96 g/cm³. The space group, from systematic absences and subsequent structure analysis, is *Fm2m* (No. 42).

Intensities were estimated visually from integrated Weissenberg photographs around the *b* and *c* axes, taken with CuK α radiation using the multi-film technique. The three-dimensional refinement was based on the *h0l*–*h3l* and *hk0*–*hk1* data. 119 out of 132 *h0l*, 115 out of 117 *h1l*, 113 out of 120 *h2l*, 88 out of 93 *h3l*, 31 out of 32 *hk0*, and 23 out of 26 *hkl* reflections, in all 429 out of 455 independent *h0l*–*h3l* and *hk0*–*hk1* reflections, accessible with CuK α radiation, were observed with measurable intensities. Three different crystals with approximately prism shape were used; the crystal used for the collection of the *h0l* data had cross-section 0.05 \times 0.11 mm² and length 0.11 mm. The corresponding dimensions of the crystals used for the *h1l*–*h3l* and for the *hk0*–*hkl* data were 0.09 \times 0.08 mm² and 0.125 mm, and 0.08 \times 0.13 mm² and 0.08 mm, respectively. The linear absorption coefficient, $\mu = 232$ cm⁻¹.

The intensities were corrected for absorption by the method of Coppens *et al.*⁵ A sub-division of 10, 4, and 14 Gaussian points along the *a*, *b*, and *c* axes, respectively, were used for all three crystals.

The computer programs used for data reduction and absorption correction were made available by the Chemical Department of X-Ray Crystallography, Weizmann Institute of Science, Rehovoth, Israel, and modified for use on the IBM 360/50H computer by Dr. D. Rabinovich.

THE STRUCTURE ANALYSIS

With eight rubidium ions and eight triselenocyanate ions in the unit cell, and four water molecules, the space group *Fm2m*, if correct, would demand that the ions, and the water molecule, lie in special positions. The structure of the potassium salt, which has space group *F2* and similar although monoclinic unit cell, indicated that in the rubidium salt, the triselenocyanate ion may lie across a mirror plane, with the middle selenocyanate group in the plane. This was confirmed through the structure analysis.

Approximate *x* and *z* coordinates of the rubidium ion and of the selenium atoms were found from the *h0l* Patterson map, by reference to the structure of K(SeCN)₃· $\frac{1}{2}$ H₂O.² The carbon and nitrogen atoms were placed partly on the basis of subsequent *h0l* Fourier maps, and partly from the analogy with the potassium salt.

The three-dimensional refinement was carried out on the IBM 360/50H computer, using a full-matrix least squares program with weighting scheme $1/(1 + AF_o + BF_o^2)$. The values used for *A* and *B* were -1.2×10^{-2} and 6×10^{-5} , respectively. Refinement with isotropic temperature factors brought the reliability index, *R*, to 0.111. The observed structure factors were then corrected for secondary extinction by the method of Zachariasen,⁶ neglecting the absorption term, since this correction had been carried out earlier: $F_{\text{corr}} = KF_o(1 + \beta CI_o)$, where $\beta = 2(1 + \cos^4 2\theta)/(1 + \cos^2 2\theta)^2$, and *C* was found to be 1.1×10^{-7} . The intensities of reflections that occurred more than once in the data set, were averaged, and such reflections thereafter included only once.

The final refinement, based on the corrected observed structure factors, and with anisotropic temperature factors for rubidium and selenium, brought the reliability index, R , down to 0.083, with unobserved reflections included if $|F_c|$ exceeds the observable limit.

The programs used for the least squares refinement, extinction correction, calculation of distances and angles, and least squares planes, were written by K. Maartmann-Moe of this Institute.

The calculated structure factors were based on atomic scattering factors, given in the *International Tables* (Ref. 7, Table 3.3.1A). The scattering factors for selenium and rubidium were corrected for anomalous dispersion, real and imaginary parts (Ref. 7, Table 3.3.2A), by taking the amplitude of f as the corrected value.

The final atomic coordinates and temperature parameters are listed in Tables 1 and 2, and the structure factors in Table 3.

Table 1. Atomic coordinates for rubidium triselenocyanate hemihydrate, in fractions of orthorhombic cell edges, with origin on $m2m$. Isotropic temperature parameters (\AA^2) in the form $\exp - [B(\sin^2\theta/\lambda^2)]$. Standard deviations from least squares are given in parentheses.

	x	y	z	B
Rb	0.14340(20)	0.2384(17)	0	
Se ₁	0.15892(12)	0.0128(14)	0.19247(10)	
Se ₂	0	0	0.19401(14)	
C ₁	0.1688(11)	-0.165(5)	0.1230(9)	2.5(4)
C ₂	0	0.232(10)	0.1310(14)	3.3(6)
N ₁	0.1768(11)	-0.276(7)	0.0778(9)	4.1(4)
N ₂	0	0.378(6)	0.0905(12)	3.2(5)
O	0	-0.147(9)	0	4.7(9)

Table 2. Anisotropic temperature parameters (\AA^2) in the form $\exp - [B_{11}(h^2/4a^2) + \dots + B_{23}(kl/4bc) + \dots]$. Standard deviations are given in parentheses.

	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Rb	3.88(11)	2.89(18)	3.95(12)	0	0	-0.38(17)
Se ₁	2.73(7)	4.86(18)	3.08(8)	-0.48(14)	-0.26(8)	-0.01(13)
Se ₂	3.44(11)	2.94(19)	2.66(10)	-0.07(18)	0	0

THE TRISELENOCYANATE ION

Bond lengths and angles in the triselenocyanate ion, based on the atomic coordinates in Table 1, are listed in Table 4. The uncertainties in cell dimensions are taken into account in the given standard deviations. In Table 4, a prime denotes an atom located at (\bar{x}, y, z) relative to the unprimed one; the primed atom is related to the unprimed one through the operation of the mirror plane parallel to (100) passing through the middle selenium atom, Se₂.

In the triselenocyanate ion, the Se-Se-Se angle is 176.9(3)°, and the three-selenium sequence is thus very nearly linear. The Se-Se bond length is 2.656(3) Å. In contrast to the present salt, where mirror plane symmetry makes the two Se-Se bonds equal, the three-selenium sequence in the corre-

Table 3. Observed and calculated structure factors. Unobserved reflections are indicated by a minus sign on $F(O)$.

F	K	L	F(C)	F(C)	F	K	L	F(O)	F(C)	F	K	L	F(O)	F(C)	F	K	L	F(O)	F(C)
0	0	2	181	183	12	0	24	35	49	9	1	9	18	11	4	2	24	37	41
0	0	4	195	195	14	0	0	200	182	9	1	11	59	85	4	2	26	23	27
0	0	4	456	561	14	0	2	-125	9	1	13	93	83	6	2	20	222	233	3
0	0	4	295	367	14	0	4	79	103	9	1	15	46	40	6	2	2	370	424
0	0	10	621	704	14	0	6	138	135	9	1	17	21	21	6	2	4	47	42
0	0	12	27	9	14	0	8	32	16	9	1	19	51	49	6	2	6	155	144
0	0	14	45	52	14	0	10	146	150	9	1	21	48	51	6	2	8	407	422
0	0	16	394	426	14	0	12	-16	13	9	1	23	15	19	6	2	10	218	214
0	0	18	215	224	14	0	14	32	34	9	1	25	-10	5	6	2	12	194	177
0	0	20	195	169	14	0	16	92	63	11	1	1	130	122	6	2	14	153	145
0	0	22	65	70	14	0	18	28	24	11	1	3	146	143	6	2	16	138	128
0	0	24	46	41	14	0	20	73	80	11	1	5	137	134	6	2	18	211	216
0	0	26	173	177	16	0	0	81	77	11	1	7	99	84	6	2	20	91	91
0	0	28	25	74	16	0	2	47	52	11	1	9	61	78	6	2	22	28	26
0	0	30	85	64	16	0	4	29	29	11	1	11	105	85	6	2	24	95	109
0	0	32	27	22	16	0	6	65	65	11	1	13	123	110	6	2	26	59	72
0	0	34	-7	-1	16	0	8	49	52	11	1	15	88	86	8	2	0	42	38
0	0	36	37	35	16	0	10	55	61	11	1	17	67	52	8	2	2	146	137
0	0	38	10	19	16	0	12	16	16	11	1	19	44	43	8	2	4	79	64
0	0	40	51	52	16	0	14	16	18	11	1	21	39	40	8	2	6	72	59
0	0	42	14	15	16	0	16	44	52	11	1	23	37	42	8	2	8	173	160
0	0	44	15	22	16	0	18	21	23	13	1	1	131	121	8	2	10	37	27
0	0	46	46	45	18	0	0	111	110	13	1	3	213	223	8	2	12	56	80
0	0	48	20	34	18	0	2	111	119	13	1	5	234	261	8	2	14	55	44
0	0	50	-16	5	18	0	4	42	42	13	1	7	140	132	8	2	16	-21	14
0	0	52	24	-16	12	0	6	24	22	13	1	9	47	39	8	2	18	83	85
0	0	54	-14	7	18	0	8	103	119	13	1	11	155	151	8	2	20	-18	7
0	0	56	28	23	16	0	10	56	62	13	1	13	162	183	8	2	22	38	38
0	0	58	278	242	18	0	12	54	63	13	1	15	140	144	8	2	24	20	26
0	0	60	185	135	18	0	14	42	46	13	1	17	33	28	8	2	26	66	66
0	0	62	202	203	20	0	0	99	87	13	1	19	55	56	10	2	2	146	140
0	0	64	210	217	20	0	2	32	34	13	1	21	55	99	10	2	4	100	91
0	0	66	86	86	20	0	4	30	36	15	1	1	62	63	10	2	6	67	53
0	0	68	106	162	20	0	6	48	56	15	1	3	57	58	10	2	8	143	131
0	0	70	101	103	20	0	8	35	40	15	1	5	81	28	10	2	10	61	61
0	0	72	14	70	20	0	10	56	72	15	1	7	48	42	10	2	12	93	82
0	0	74	123	126	1	1	1	198	223	15	1	9	47	44	10	2	14	75	69
0	0	76	56	56	1	1	3	382	400	15	1	11	33	34	10	2	16	-20	19
0	0	78	55	47	1	1	5	515	482	15	1	13	40	45	10	2	18	70	73
0	0	80	47	42	1	1	7	258	222	15	1	15	26	30	10	2	20	31	29
0	0	82	18	20	1	1	9	122	103	15	1	17	16	20	10	2	22	21	24
0	0	84	56	45	1	1	11	252	231	15	1	19	20	24	12	2	0	226	212
0	0	86	22	24	1	1	13	306	266	17	1	1	59	54	12	2	2	167	163
0	0	88	891	706	1	1	15	235	223	17	1	3	52	47	12	2	4	77	67
0	0	90	255	221	1	1	17	63	50	17	1	5	46	43	12	2	6	143	140
0	0	92	182	175	1	1	19	90	66	17	1	7	37	34	12	2	8	97	100
0	0	94	390	332	1	1	21	150	147	17	1	9	35	37	12	2	10	177	176
0	0	96	345	303	1	1	23	116	119	17	1	11	39	37	12	2	12	55	50
0	0	98	477	405	1	1	25	52	57	17	1	13	32	35	12	2	14	53	45
0	0	100	66	59	1	1	27	17	23	17	1	15	27	34	12	2	16	105	110
0	0	102	-15	7	3	1	1	137	140	15	1	1	53	47	13	2	18	97	100
0	0	104	322	324	3	1	3	302	322	19	1	3	104	111	12	2	0	65	97
0	0	106	227	211	3	1	5	390	354	19	1	5	105	123	12	2	2	-8	0
0	0	108	146	144	3	1	7	221	213	19	1	7	64	66	14	2	0	44	36
0	0	110	46	43	3	1	9	146	129	19	1	9	-11	11	14	2	2	140	125
0	0	112	55	49	3	1	11	226	158	19	1	11	62	70	14	2	4	60	50
0	0	114	136	134	3	1	13	173	154	21	1	1	28	30	14	2	6	42	37
0	0	116	227	212	3	1	15	119	102	0	2	2	472	609	14	2	8	133	138
0	0	118	-13	13	3	1	17	105	87	0	2	4	91	85	14	2	10	33	23
0	0	120	157	136	3	1	19	116	103	0	2	6	143	127	14	2	12	77	73
0	0	122	195	171	3	1	21	198	162	0	2	8	551	574	14	2	14	52	45
0	0	124	-14	15	3	1	23	38	36	0	2	10	218	238	14	2	16	15	18
0	0	126	152	172	3	1	25	16	20	0	2	12	271	262	14	2	18	71	78
0	0	128	24	17	3	1	27	34	40	0	2	14	237	211	16	2	0	61	56
0	0	130	54	45	5	1	1	125	128	0	2	16	130	124	16	2	2	59	51
0	0	132	16	15	5	1	3	247	263	0	2	18	271	282	16	2	4	-18	14
0	0	134	25	19	5	1	5	278	252	0	2	20	48	89	16	2	6	20	21
0	0	136	50	43	5	1	7	127	116	0	2	22	53	48	16	2	8	64	58
0	0	138	28	27	5	1	9	47	36	0	2	24	119	140	16	2	10	34	34
0	0	140	-14	3	5	1	11	160	136	0	2	26	64	74	16	2	12	24	23
0	0	142	31	33	5	1	13	214	200	2	2	0	120	122	16	2	14	20	18
10	0	0	155	154	5	1	15	155	147	2	2	2	42	37	16	2	16	22	25
10	0	2	31	27	5	1	17	35	30	2	2	4	56	54	18	2	0	119	113
10	0	4	131	133	5	1	19	63	56	2	2	6	25	17	18	2	2	47	42
10	0	6	184	173	5	1	21	53	50	2	2	8	48	38	18	2	4	54	51
10	0	8	-16	6	5	1	23	81	80	2	2	10	109	87	18	2	6	76	79
10	0	10	173	143	5	1	25	36	42	2	2	12	62	48	18	2	8	66	62
10	0	12	56	81	5	1	27	14	19	2	2	14	42	31	18	2	10	83	82
10	0	14	40	25	7	1	1	230	244	2	2	16	45	30	18	2	12	-5	2
10	0	16	125	114	7	1	3	349	363	2	2	18	24	16	20	2	0	45	44
10	0	18	20	13	7	1	5	414	435	2	2	20	38	34	20	2	2	53	57
10	0	20	62	53	7	1	7	205	224	2	2	22	22	16	1	3	1	77	89
10	0	22	35	31	7	1	9	130	123	2	2	24	-16	10	1	3	116	247	
10	0	24	-11	1	7	1	11	250	242	2	2	26	27	26	1	3	5	201	211
12	0	0	351	353	7	1	13	252	278	4	2	0	147	146	1	3	7	225	211
12	0	2	206	216	7	1	15	242	225	4	2	2	170	167	1	3	9	111	89
12	0	4	26																

Table 4. Dimensions of the triselenocyanate ion. Bond lengths (Å) and angles (°). Standard deviations are given in parentheses.

$\text{Se}_1-\text{Se}_2 = 2.656(3)$	$\angle \text{Se}_1-\text{Se}_2-\text{Se}_1' = 176.9(3)$
$\text{Se}_1-\text{C}_1 = 1.81(2)$	$\angle \text{Se}_1-\text{C}_1-\text{N}_1 = 178.4(17)$
$\text{Se}_2-\text{C}_2 = 1.82(4)$	$\angle \text{Se}_2-\text{C}_2-\text{N}_2 = 179.3(30)$
$\text{C}_1-\text{N}_1 = 1.17(3)$	$\angle \text{Se}_1-\text{Se}_2-\text{C}_2 = 88.58(15)$
$\text{C}_2-\text{N}_2 = 1.16(5)$	$\angle \text{Se}_2-\text{Se}_1-\text{C}_1 = 95.3(8)$

sponding potassium salt² is slightly unsymmetrical, with Se-Se-Se bond angle of 176.0° and Se-Se bond lengths of 2.689 and 2.648 Å. The total length of the three-selenium sequence (the sum of the lengths of the two bonds) is 5.337 Å in the potassium salt and 5.312 Å in the rubidium salt, the mean

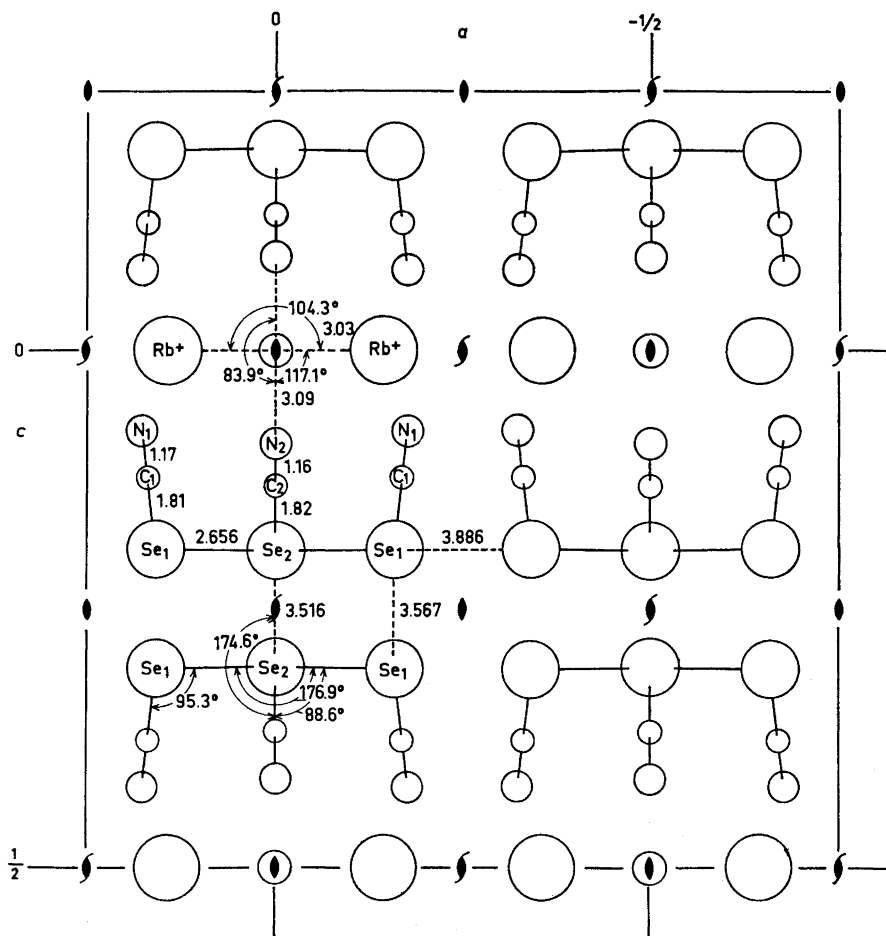


Fig. 1. Rubidium triselenocyanate hemihydrate as seen along the *b* crystal axis.

value being 5.325 Å. The same mean total length is found for the very nearly linear, unsymmetrical three-selenium sequence in two salts of the triselenourea ion,⁸ the dichloride and dibromide.

Thus, from four structure analyses of linear three-selenium systems, one symmetrical and three unsymmetrical, it is found that the mean value of the Se-Se bond length is 2.66 Å. This is 0.32 Å longer than a single covalent selenium-selenium bond.⁹

The Se-Se-C bond angle at the middle selenium atom, Se₂, is 88.58(15)°, and the Se-Se-C bond angle at the terminal selenium atom, Se₁, is 95.3(8)°.

Each of the selenocyanate groups of the ion is linear within the error; the found values for the Se-C-N angles are 178.4(17)° and 179.3(30)°. The Se-C bonds are 1.81(2) and 1.82(4) Å, and the C-N bonds 1.17(3) and 1.16(3) Å. Within the accuracy of the analyses, these values are the same as found in the corresponding potassium salt,² and also for the selenocyanate ion in the crystals of potassium selenocyanate.¹⁰

The atoms of the terminal selenocyanate groups and the middle selenium atom, Se₂, are approximately co-planar, the largest deviation of an atom from a least squares plane being 0.05 Å (*cf.* Table 6). So are the atoms of the middle selenocyanate group and the terminal selenium atoms, Se₁ and Se₁', the largest deviation of an atom from a least squares plane being 0.02 Å. These two planes make an angle of 65.0° with each other.

Tables 5. Close interionic selenium-selenium contacts. Distances (Å) and angles (°). Standard deviations are given in parentheses.

Se ₂ ...Se ₂ ' = 3.516(4)	∠C ₁ -S ₁ ...Se ₁ ' = 164.9(9)
Se ₂ ...Se ₂ ''' = 3.516(4)	∠C ₁ -Se ₁ ...Se ₁ ''' = 108.8(8)
Se ₁ ...Se ₁ ' = 3.567(8)	∠C ₂ -Se ₂ ...Se ₂ ' = 98.6(14)
Se ₁ ...Se ₁ ''' = 3.567(8)	∠C ₂ -Se ₂ ...Se ₂ ''' = 174.6(14)

Table 6. Distances from least squares planes. The equations of the planes were calculated with the selenium coordinates given six times the weight of the carbon and nitrogen coordinates, and refer to the axes of the unit cell, with coordinates Y and Z in Å.

Plane through Se₁C₁N₁, Se₂, and Se₁'C₁'N₁':

$$0.8863 Y - 0.4632 Z + 2.0023 = 0$$

Se ₁	0.024 Å	C ₁	-0.003 Å	N ₁	0.000 Å
Se ₂	-0.047				

Plane through Se₁, Se₂C₂N₂, and Se₁':

$$0.7943 Y + 0.6075 Z - 2.7068 = 0$$

Se ₁	-0.018 Å	C ₂	0.000 Å	N ₂	0.002 Å
Se ₂	0.009				

Plane through C₂, Se₁Se₂Se₁', and Se₂''':

$$0.7293 Y + 0.6842 Z - 3.0274 = 0$$

C ₂	-0.165 Å	Se ₁	0.021 Å	Se ₂ '''	0.015 Å
		Se ₂	0.000		

INTERIONIC SELENIUM-SELENIUM CONTACTS

Each selenium atom in the three-selenium sequence has two close selenium-selenium contacts to atoms in adjacent triselenocyanate ions. The relevant data are listed in Table 5. In the table, a double-prime denotes an atom located at $(x, \frac{1}{2} + y, \frac{1}{2} - z)$ relative to the unprimed one, and a triple-prime denotes an atom located at $(x, y - \frac{1}{2}, \frac{1}{2} - z)$ relative to the unprimed one; the double-primed and triple-primed atoms are both related to the unprimed ones through the operation of the mirror plane parallel to (100), passing through the middle selenium atom, Se_2 , followed by the operation of the screw axis parallel to b near Se_2 .

Table 5 shows close $\text{Se}_2 \cdots \text{Se}_2''$ and $\text{Se}_2 \cdots \text{Se}_2'''$ contacts of 3.516(4) Å, and $\text{Se}_1 \cdots \text{Se}_1''$ and $\text{Se}_1 \cdots \text{Se}_1'''$ contacts of 3.567(8) Å. For comparison, the Pauling⁹ van der Waals radius of selenium is 2.00 Å.

The Se_2''' atom approaches the fourth coordination site of square-planar four-coordination at Se_2 . Thus, the $\text{Se}_1\text{Se}_2\text{Se}_1'$, Se_2''' , and C_2 atoms lie approximately in the same plane (cf. Table 6), the $\text{Se}_1 - \text{Se}_2 - \text{Se}_1'$ angle is 176.9°, the $\text{Se}_2 - \text{C}_2$ bond bisects the $\text{Se}_1 - \text{Se}_2 - \text{Se}_1'$ angle, and the $\text{C}_2 - \text{Se}_2 \cdots \text{Se}_2'''$ angle is 174.6°. The same structural feature occurs in the crystals of the potassium salt.²

The $\text{Se}_2 \cdots \text{Se}_2''$ contact, also 3.516 Å, occurs at a $\text{C}_2 - \text{Se}_2 \cdots \text{Se}_2''$ angle of 98.6°.

The two close contacts of the terminal selenium atoms occur at $\text{C} - \text{Se} \cdots \text{Se}$ angles of 164.9° and 108.8°.

THE ENVIRONMENT OF THE RUBIDIUM ION AND THE WATER MOLECULE

The water molecule lies in position of mm symmetry at $(0, y, 0)$. It is surrounded by two rubidium ions at distances of 3.03(3) Å and a $\text{Rb} \cdots \text{O} \cdots \text{Rb}$ angle of 104.3(10)°, and by two N_2 nitrogen atoms at distances of 3.09(5) Å and a $\text{N} \cdots \text{O} \cdots \text{N}$ angle of 83.9(11)°. The latter contacts probably involve weak $\text{O} - \text{H} \cdots \text{H}$ hydrogen bonds. The arrangement around the water molecule is approximately tetrahedral, the $\text{Rb} \cdots \text{O} \cdots \text{N}$ angle being 117.2(6)°.

Table 7. Distances from the rubidium ion to neighbouring atoms. Standard deviation, 0.03 Å.

$\text{Rb} \cdots \text{N}_1(x, y, z)$	= 3.10 Å	$\text{Rb} \cdots \text{N}_2(x, y, z)$	= 3.23 Å
$\text{Rb} \cdots \text{N}_1(x, 1 + y, z)$	= 3.00	$\text{Rb} \cdots \text{N}_2(x, y, \bar{z})$	= 3.23
$\text{Rb} \cdots \text{N}_1(x, y, \bar{z})$	= 3.10	$\text{Rb} \cdots \text{O}$	= 3.03
$\text{Rb} \cdots \text{N}_1(x, 1 + y, \bar{z})$	= 3.00		

The closest contacts of the rubidium ion are listed in Table 7 and shown in Fig. 2. The rubidium ion is surrounded by six nitrogen atoms at distances ranging from 3.00 to 3.23 Å, and by one oxygen atom, at 3.03 Å. Four of the six nitrogen atoms, at $\text{Rb} \cdots \text{N} = 3.00$ and 3.10 Å, lie exactly in a plane, parallel to (100), at $x = 0.1768$. The two remaining nitrogen atoms, at $\text{Rb} \cdots \text{N} = 3.23$ Å,

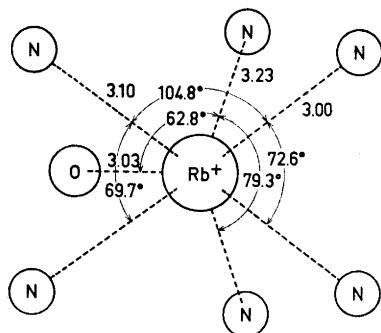


Fig. 2. The surroundings of the rubidium ion in rubidium triselenocyanate hemihydrate, as seen along the a crystal axis.

and the oxygen atom, lie in the plane (100) at $x=0$. The rubidium ion lies 0.54 Å from the former plane and 2.40 Å from the latter plane, between the planes. The $\text{Rb}\cdots\text{O}$ distance is in the normal range (cf. Ref. 6, p. 259), and so are the $\text{Rb}\cdots\text{N}$ distances, the sum of the $\text{Rb}\cdots\text{N}$ ionic radii being 3.19 Å.⁹

REFERENCES

1. Verneuil, A. *Ann. Chim. Phys.* [6] **9** (1886) 289.
2. Hauge, S. and Sletten, J. *Acta Chem. Scand.* **25** (1971) 3094.
3. Birckenback, L. and Kellermann, K. *Ber.* **58** (1925) 2377.
4. Hauge, S. *Acta Chem. Scand.* **25** (1971) 3081.
5. Coppens, P., Leiserowitz, L. and Rabinovich, D. *Acta Cryst.* **18** (1965) 1035.
6. Zachariasen, W. H. *Acta Cryst.* **16** (1963) 1139.
7. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
8. Hauge, S., Opedal, O. and Aarskog, J. *Acta Chem. Scand.* **24** (1970) 1107.
9. Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, Ithaca, New York 1960.
10. Swank, D. D. and Willett, R. D. *Inorg. Chem.* **4** (1965) 499.

Received December 21, 1970.