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The Crystal Structure of Potassium Triselenocyanate Hemihydrate

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The crystal structure of potassium triselenocyanate hemihydrate, $K(SeCN)_3 \cdot \frac{1}{2}H_2O$, has been determined by X-ray methods, and refined by full-matrix least squares procedures. The crystals are monoclinic, space group $F2$ (No. 5), with $a = 16.988(8)$ Å, $b = 4.443(3)$ Å, $c = 23.590(10)$ Å, $\beta = 95.70(5)°$, and eight formula units per unit cell.

In the triselenocyanate ion, the three-selenium sequence is very nearly linear, with bond lengths, $Se_1 - Se_2 = 2.689(4)$ Å, $Se_2 - Se_3 = 2.648(4)$ Å, and $Se_1 - Se_2 - Se_3$ bond angle, 176.0(3)°. The selenium–selenium bonds are 0.35 Å and 0.31 Å, respectively, longer than single covalent selenium–selenium bonds.

Each of the three selenocyanate groups is linear within the error. The terminal selenocyanate groups and the middle selenium atom, Se_2, lie approximately in the same plane. This plane makes an angle of 57.4° with a plane through the middle selenocyanate group and the terminal selenium atoms.

Potassium triselenocyanate hemihydrate, $K(SeCN)_3 \cdot \frac{1}{2}H_2O$, was first isolated by Verneuil [1] in 1884–1886, although by him described without crystal water. Its crystal structure analysis, reported here, is the first of a substance containing three selenium atoms in a linear three-centre arrangement.

CRYSTAL DATA

Preparative and crystallographic data on potassium triselenocyanate hemihydrate and other triselenocyanates have been reported earlier.[2]

The salt, $K(SeCN)_3 \cdot \frac{1}{2}H_2O$, forms long, brown, monoclinic prisms elongated along the b axis, with $a = 16.988(8)$ Å, $b = 4.443(3)$ Å, $c = 23.590(10)$ Å, and $\beta = 95.70(5)°$. The unit cell dimensions were determined from zero-layer Weissenberg photographs around the a and b axes, and evaluated by means of a least squares program.

There are eight formula units per unit cell; density, calc. 2.72, found 2.74 g/cm^3. The space group, from systematic absences and subsequent structure analysis, is $F2$ (No. 5). The F-centered setting has been chosen in order to

bring out the analogy with the crystals of the rubidium salt,[2,4] the space group of which is $Fm2m$ (No. 42). In the conventional $C2$ setting, the potassium salt has $c = 13.834$ Å, $\beta = 121.95°$, and four formula units per unit cell.

Intensities were estimated visually from Weissenberg photographs, integrated in vertical direction, and taken with Cu$K\alpha$ radiation. The structure was solved[3] from zero-layer photographs around the b axis and the short ac-diagonal (the c axis in the $C2$ setting). The three-dimensional refinement was based on hkl data with $k = 0-3$. 206 out of 256 $h0l$, 220 out of 239 $h1l$, 198 out of 221 $h2l$, and 168 out of 198 $h3l$ reflections, in all 792 out of 898 $h0l-h3l$ reflections, accessible with Cu$K\alpha$ radiation, were observed with measurable intensities. The crystal used was a small prism, with cross-section 0.023×0.031 mm^2 and length 0.192 mm. The linear absorption coefficient, $\mu = 209$ cm^{-1}.

The intensities were corrected for spot extension by the method of Phillips.[5] They were corrected for absorption by the method of Coppens *et al.*,[6] using a sub-division of 10, 4, and 14 Gaussian points, respectively, along the a, b, and c axis.

The computer programs used for data reduction and adsorption 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

The approximate positions of the selenium atoms in the b axis and short ac-diagonal projections were found from the Patterson maps. The carbon and nitrogen atoms were placed partly on the basis of subsequent Fourier maps, and partly from the known dimensions of the selenocyanate group. The projections were refined through difference syntheses.

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 0.114. The observed structure factors were then corrected for secondary extinction by a computer program, using the method of Zachariasen,[7] neglecting the absorption term, since this correction had been carried out earlier: $F_{corr} = K\, F_o(1 + \beta C I_o)$, where $\beta = 2(1 + \cos^4 2\theta)/(1 + \cos^2 2\theta)^2$, and C was found to be 3.7×10^{-8}.

The final refinement, based on the corrected observed structure factors, and with anisotropic temperature factors for potassium and selenium, brought the reliability index, R, down to 0.097, 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. In the least squares program, the scale factors for the individual layers do not enter as variable parameters in the matrix, but are corrected after each refinement cycle.

The calculated structure factors were based on atomic scattering factors, given in *International Tables* (Ref. 8, Table 3.3.1A). The scattering factors

for selenium and potassium were corrected for anomalous dispersion, real and imaginary parts (Ref. 8, 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 potassium triselenocyanate hemihydrate, in fractions of monoclinic cell edges, with origin on a twofold axis. Isotropic temperature parameters (Å²) in the form $\exp-[B(\sin^2\theta/\lambda^2)]$. Standard deviations from least squares are given in parentheses.

	x	y	z	B
K	0.13785(36)	0.2494(20)	0.00722(26)	
Se_1	−0.16233(14)	0.0053(20)	0.18244(11)	
Se_2	−0.00328(15)	−0.0032(20)	0.19340(10)	
Se_3	0.15306(14)	0.0192(20)	0.19900(11)	
C_1	−0.1754(14)	−0.162(8)	0.1097(10)	2.3(5)
C_2	−0.0068(13)	0.227(8)	0.1296(9)	1.9(4)
C_3	0.1578(16)	−0.159(8)	0.1295(11)	2.6(5)
N_1	−0.1843(13)	−0.256(8)	0.0658(9)	3.0(4)
N_2	−0.0093(15)	0.368(8)	0.0896(10)	3.3(5)
N_3	0.1592(13)	−0.265(8)	0.0866(9)	2.8(4)
O	0	−0.151(8)	0	3.0(6)

Table 2. Anisotropic temperature parameters (Å²) in the form $\exp-[B_{11}(h^2/4a^2)+\cdots+B_{23}(kl/4bc)+\cdots]$. Standard deviations are given in parentheses.

	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
K	3.53(24)	0.73(44)	3.74(24)	−0.16(23)	−0.22(21)	−0.04(25)
Se_1	2.15(8)	2.86(18)	2.80(9)	−0.39(18)	−0.40(8)	−0.30(17)
Se_2	3.04(9)	1.01(15)	2.09(9)	−0.03(14)	0.24(6)	−0.10(14)
Se_3	2.23(9)	2.50(18)	2.69(9)	−0.38(17)	−0.08(8)	−0.02(17)

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 the cell dimensions are taken into account in the given standard deviations.

In the triselenocyanate ion, the $Se_1-Se_2-Se_3$ angle is 176.0(3)°, and the three-selenium sequence is thus very nearly linear. The Se_1-Se_2 and Se_2-Se_3 bond lengths are 2.689(4) Å and 2.648(4) Å, respectively. The difference in bond lengths amounts to 10σ and is thus significant.

The selenium-selenium bonds in the linear three-centre sequence of the slightly unsymmetrical triselenocyanate ion in the potassium salt are thus 0.35 Å and 0.31 Å longer than single covalent selenium-selenium bonds,[9] 2.34 Å. In centrosymmetric square-planar tellurium(II) complexes,[10,11] the tellurium-ligand bonds are 0.27 Å longer than single bonds. In the triiodide ion,[12] the iodine-iodine bonds are 0.30 Å longer than single bonds.

The Se−Se−C bond angles at the middle selenium atom, Se_2, are 87.8(7)° and 88.3(7)°, and are thus equal within the error. So are the Se−Se−C bond angles at the terminal selenium atoms, Se_1 and Se_3: 96.3(8)° and 94.1(9)°.

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

H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)
0	0	2	166	310	12	0	20	39	34	10	0	-8	109	111	5	1	15	151	169	3	1-11	97	83
0	0	4	45	50	12	0	22	72	70	10	0-10		133	134	5	1	17	41	44	3	1-13	58	51
0	0	6	383	397	14	0	0	193	180	10	0-12		46	41	5	1	19	138	167	3	1-15	38	33
0	0	8	394	413	14	0	2	38	28	10	0-14		-29	31	5	1	21	188	209	3	1-17	25	30
0	0	10	487	565	14	0	4	-30	17	10	0-16		89	85	5	1	23	135	143	3	1-19	39	34
0	0	12	63	45	14	0	6	109	98	10	0-18		79	73	5	1	25	36	27	3	1-21	43	39
0	0	14	63	55	14	0	8	-30	1	10	0-20		-30	19	5	1	27	51	73	3	1-23	48	57
0	0	16	322	329	14	0	10	86	78	10	0-22		-28	6	7	1	1	297	292	3	1-25	39	40
0	0	18	219	208	14	0	12	-29	13	10	0-24		-25	20	7	1	3	435	377	3	1-27	-13	11
0	0	20	129	119	14	0	14	62	58	10	0-26		-20	21	7	1	5	382	338	3	1-29	26	42
0	0	22	71	48	14	0	16	-25	7	12	0	-2	324	323	7	1	7	122	112	5	1 -1	133	110
0	0	24	72	57	14	0	18	-21	0	12	0	-4	-26	5	7	1	9	96	89	5	1 -3	227	190
0	0	26	103	88	14	0	20	39	38	12	0	-6	51	40	7	1	11	175	175	5	1 -5	261	221
0	0	28	61	55	16	0	0	77	64	12	0	-8	174	177	7	1	13	160	172	5	1 -7	120	91
0	0	30	30	26	16	0	2	45	42	12	0-10		154	164	7	1	15	103	117	5	1 -9	51	37
2	0	0	80	53	16	0	4	57	51	12	0-12		115	107	7	1	17	26	32	5	1-11	98	86
2	0	2	46	44	16	0	6	82	77	12	0-14		39	32	7	1	19	29	32	5	1-13	46	50
2	0	4	-13	5	16	0	8	61	55	12	0-16		42	42	7	1	21	37	52	5	1-15	55	50
2	0	6	48	50	16	0	10	-27	18	12	0-18		111	102	7	1	23	40	42	5	1-17	65	60
2	0	8	80	90	16	0	12	34	29	12	0-20		-28	13	7	1	25	34	37	5	1-19	68	63
2	0	10	92	94	16	0	14	30	27	12	0-22		-25	8	9	1	1	158	122	5	1-21	63	61
2	0	12	55	52	16	0	16	-19	5	12	0-24		-21	9	9	1	3	179	182	5	1-23	-18	14
2	0	14	47	42	16	0	18	-13	4	12	0-26		-16	10	9	1	5	152	116	5	1-25	-16	12
2	0	16	175	171	18	0	0	113	111	14	0	-2	125	112	9	1	7	67	54	5	1-27	28	41
2	0	18	34	23	18	0	2	47	39	14	0	-4	131	125	9	1	9	81	76	5	1-29	21	42
2	0	20	-30	3	18	0	4	77	72	14	0	-6	92	90	9	1	11	119	129	7	1 -1	143	121
2	0	22	68	47	18	0	6	102	90	14	0	-8	140	130	9	1	13	86	88	7	1 -3	443	371
2	0	24	55	44	18	0	8	146	151	14	0-10		223	228	9	1	15	21	22	7	1 -5	547	494
2	0	26	81	73	18	0	10	65	61	14	0-12		121	123	9	1	17	39	47	7	1 -7	325	295
2	0	28	33	27	18	0	12	-18	6	14	0-14		-30	15	9	1	19	54	64	7	1 -9	46	39
4	0	0	160	166	18	0	14	85	110	14	0-16		145	147	9	1	21	41	46	7	1-11	262	245
4	0	2	61	61	20	0	0	97	94	14	0-18		180	175	9	1	23	-13	6	7	1-13	360	371
4	0	4	86	91	20	0	2	28	28	14	0-20		123	122	11	1	1	109	90	7	1-15	275	290
4	0	6	94	94	20	0	4	34	30	14	0-22		-21	5	11	1	3	186	154	7	1-17	56	48
4	0	8	110	110	20	0	6	61	62	14	0-24		51	49	11	1	5	177	145	7	1-19	124	122
4	0	10	57	54	20	0	8	40	37	16	0	-2	118	113	11	1	7	54	44	7	1-21	183	191
4	0	12	74	69	2	0	-2	55	67	16	0	-4	49	38	11	1	9	77	69	7	1-23	182	157
4	0	14	66	52	2	0	-4	29	26	16	0	-6	-30	2	11	1	11	144	163	7	1-25	56	71
4	0	16	139	125	2	0	-6	104	110	16	0	-8	84	87	11	1	13	147	179	7	1-27	14	33
4	0	18	122	153	2	0	-8	118	123	16	0-10		53	55	11	1	15	74	88	9	1 -1	50	40
4	0	20	33	28	2	0	-10	231	268	16	0-12		57	56	11	1	17	48	58	9	1 -3	145	112
4	0	22	34	22	2	0	-12	61	52	16	0-14		-28	29	11	1	19	86	118	9	1 -5	116	92
4	0	24	102	83	2	0	-14	-24	15	16	0-16		-26	22	11	1	21	109	125	9	1 -7	56	46
4	0	26	136	122	2	0	-16	244	247	16	0-18		48	48	11	1	23	68	76	9	1 -9	57	41
4	0	28	68	61	2	0	-18	211	202	16	0-20		30	27	13	1	1	236	198	9	1-11	33	26
6	0	0	737	818	2	0	-20	137	122	16	0-22		-15	1	13	1	3	338	276	9	1-13	52	39
6	0	2	169	172	2	0	-22	63	52	18	0	-2	152	156	13	1	5	236	217	9	1-15	73	63
6	0	4	26	23	2	0	-24	95	79	18	0	-4	-28	1	13	1	7	55	48	9	1-17	44	38
6	0	6	339	363	2	0	-26	190	178	18	0	-6	-27	12	13	1	9	87	86	9	1-19	-19	11
6	0	8	397	409	2	0	-28	96	86	18	0	-8	56	50	13	1	11	141	160	9	1-21	67	66
6	0	10	382	429	2	0	-30	22	16	18	0-10		50	46	13	1	13	118	139	9	1-23	76	64
6	0	12	-26	9	4	0	-2	17	4	18	0-12		41	37	13	1	15	63	76	9	1-25	45	53
6	0	14	124	115	4	0	-4	84	100	18	0-14		-23	10	13	1	17	29	33	9	1-27	-10	10
6	0	16	312	339	4	0	-6	134	145	18	0-16		-20	2	13	1	19	53	52	11	1 -1	95	78
6	0	18	197	180	4	0	-8	79	88	18	0-18		23	22	13	1	21	56	60	11	1 -3	80	86
6	0	20	114	103	4	0	-10	184	200	20	0	-2	104	105	15	1	1	78	74	11	1 -5	93	77
6	0	22	94	84	4	0	-12	34	35	20	0	-4	74	74	15	1	3	78	80	11	1 -7	53	41
6	0	24	81	70	4	0	-14	-25	14	20	0	-6	-22	14	15	1	5	29	28	11	1 -9	48	38
6	0	26	123	112	4	0	-16	178	176	20	0	-8	88	91	15	1	7	-18	4	11	1-11	76	70
6	0	28	38	45	4	0	-18	68	53	20	0-10		99	115	15	1	9	59	69	11	1-13	57	54
8	0	0	213	218	4	0	-20	-30	3	20	0-12		84	100	15	1	11	61	77	11	1-15	40	35
8	0	2	26	17	4	0	-22	49	34	20	0-14		-14	14	15	1	13	35	49	11	1-17	30	34
8	0	4	67	69	4	0	-24	36	29	1	1	1	165	186	15	1	15	-14	12	11	1-19	44	45
8	0	6	68	62	4	0	-26	66	62	1	1	3	321	355	15	1	17	34	39	11	1-21	44	53
8	0	8	65	66	4	0	-28	-20	16	1	1	5	338	361	17	1	1	-18	20	11	1-23	25	34
8	0	10	63	56	4	0	-30	20	30	1	1	7	112	124	17	1	3	39	36	11	1-25	-12	3
8	0	12	-28	3	6	0	-2	406	415	1	1	9	42	47	17	1	5	40	42	13	1 -1	-18	11
8	0	14	90	81	6	0	-4	25	27	1	1	11	102	108	17	1	7	18	12	13	1 -3	267	211
8	0	16	82	66	6	0	-6	171	166	1	1	13	105	118	17	1	9	19	25	13	1 -5	393	315
8	0	18	-30	13	6	0	-8	288	323	1	1	15	80	92	17	1	11	52	61	13	1 -7	251	220
8	0	20	36	35	6	0	-10	348	350	1	1	17	30	31	17	1	13	59	64	13	1 -9	64	52
8	0	22	34	25	6	0	-12	127	122	1	1	19	32	29	17	1	15	21	29	13	1-11	142	126
8	0	24	66	59	6	0	-14	49	44	1	1	21	39	41	19	1	1	117	124	13	1-13	222	227
8	0	26	81	80	6	0	-16	166	170	1	1	23	-18	20	19	1	3	143	154	13	1-15	208	200
10	0	0	151	140	6	0	-18	189	187	1	1	25	22	27	19	1	5	96	105	13	1-17	56	57
10	0	2	-24	14	6	0	-20	66	65	1	1	27	26	33	19	1	7	16	12	13	1-19	56	59
10	0	4	-24	15	6	0	-22	-30	1	3	1	1	156	137	19	1	9	64	71	13	1-21	84	106
10	0	6	123	124	6	0	-24	46	37	3	1	3	263	247	1	1	-1	171	188	13	1-23	80	97
10	0	8	-27	10	6	0	-26	33	29	3	1	5	306	294	1	1	-3	599	462	15	1 -1	37	37
10	0	10	45	35	6	0	-28	47	46	3	1	7	165	152	1	1	-5	653	543	15	1 -3	-19	28
10	0	12	45	50	8	0	-2	72	66	3	1	9	89	91	1	1	-7	297	267	15	1 -5	-19	8
10	0	14	-31	21	8	0	-4	132	146	3	1	11	148	159	1	1	-9	81	68	15	1 -7	73	59
10	0	16	-30	24	8	0	-6	176	182	3	1	13	100	107	1	1-11		344	330	15	1 -9	37	38
10	0	18	88	70	8	0	-8	131	123	3	1	15	45	53	1	1-13		454	432	15	1-11	29	30
10	0	20	-26	19	8	0	-10	298	326	3	1	17	48	55	1	1-15		299	291	15	1-13	58	50
10	0	22	-23	11	8	0	-12	97	65	3	1	19	65	67	1	1-17		81	83	15	1-15	71	72
10	0	24	-62	56	8	0	-14	-27	16	3	1	21	57	46	1	1-19		185	174	15	1-17	42	43
12	0	0	326	331	8	0	-16	240	246	3	1	23	-17	22	1	1-21		231	243	15	1-19	-14	10
12	0	2	120	114	8	0	-18	220	211	3	1	25	23	34	1	1-23		175	181	15	1-21	54	62
12	0	4	105	94	8	0	-20	179	161	3	1	27	15	26	1	1-25		59	59	17	1 -1	-18	22
12	0	6	222	208	8	0	-22	32	33	5	1	1	197	156	1	1-27		33	60	17	1 -3	-18	10
12	0	8	255	259	8	0	-24	80	66	5	1	3	359	326	1	1-29		56	101	17	1 -5	31	27
12	0	10	202	193	8	0	-26	166	160	5	1	5	373	332	3	1 -1		91	77	17	1 -7	41	40
12	0	12	-30	1	8	0	-28	96	100	5	1	7	133	125	3	1 -3		312	263	17	1 -9	21	21
12	0	14	176	150	10	0	-2	102	97	5	1	9	77	69	3	1 -5		340	286	17	1-11	23	30
12	0	16	225	216	10	0	-4	77	77	5	1	11	254	241	3	1 -7		137	103	17	1-13	49	53
12	0	18	142	131	10	0	-6	79	66	5	1	13	275	334	3	1 -9		49	37	17	1-15	41	43

Table 3. Continued.

H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)
17	1	-17	-13	15	10	2	10	65	62	6	2	-26	55	55	3	3	7	90	91	1	3	-25	43	37
17	1	-15	18	20	10	2	12	23	26	8	2	-2	183	183	3	3	9	93	92	3	3	-1	37	29
19	1	-1	26	30	10	2	14	-16	23	8	2	-4	26	24	3	3	11	71	59	3	3	-3	110	117
19	1	-3	56	53	10	2	16	44	46	8	2	-6	33	25	3	3	13	83	83	3	3	-5	88	88
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19	1	-7	115	125	10	2	20	60	60	8	2	-10	174	164	3	3	17	32	40	3	3	-9	48	43
19	1	-9	42	44	10	2	22	56	44	8	2	-12	162	155	3	3	19	48	51	3	3	-11	40	32
19	1	-11	46	48	12	2	0	249	234	8	2	-14	91	86	3	3	21	-14	11	3	3	-13	41	45
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19	1	-15	79	99	12	2	4	39	37	8	2	-18	193	211	5	3	1	112	103	3	3	-17	31	34
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0	2	22	-15	11	14	2	4	37	30	10	2	-14	26	34	5	3	23	110	101	5	3	-13	65	68
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8	2	14	42	41	6	2	-4	141	142	1	3	9	28	20	1	3	-1	80	85	13	3	-19	31	29
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8	2	18	26	26	6	2	-8	300	333	1	3	13	109	96	1	3	-5	261	303	15	3	-3	-16	15
8	2	20	16	13	6	2	-10	232	255	1	3	15	59	50	1	3	-7	213	238	15	3	-5	27	38
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10	2	0	69	63	6	2	-16	134	139	1	3	21	-15	11	1	3	-13	251	258	15	3	-11	15	22
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10	2	6	-15	14	6	2	-22	20	14	3	3	1	44	29	1	3	-19	133	134	17	3	-1	-12	5
10	2	8	71	63	6	2	-24	36	29	3	3	3	132	137	1	3	-21	166	176	17	3	-3	16	21
										3	3	5	108	103	1	3	-23	136	132	17	3	-5	24	22

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

$Se_1-Se_2 = 2.689(4)$	$\angle Se_1-Se_2-Se_3 = 176.0(3)$
$Se_2-Se_3 = 2.648(4)$	$\angle Se_1-C_1-N_1 = 178.3(25)$
$Se_1-C_1 = 1.86(3)$	$\angle Se_2-C_2-N_2 = 179.2(25)$
$Se_2-C_2 = 1.82(3)$	$\angle Se_3-C_3-N_3 = 178.6(20)$
$Se_3-C_3 = 1.83(3)$	$\angle Se_2-Se_1-C_1 = 96.3(8)$
$C_1-N_1 = 1.11(4)$	$\angle Se_1-Se_2-C_2 = 87.8(7)$
$C_2-N_2 = 1.13(4)$	$\angle Se_3-Se_2-C_2 = 88.3(7)$
$C_3-N_3 = 1.12(4)$	$\angle Se_2-Se_3-C_3 = 94.1(8)$

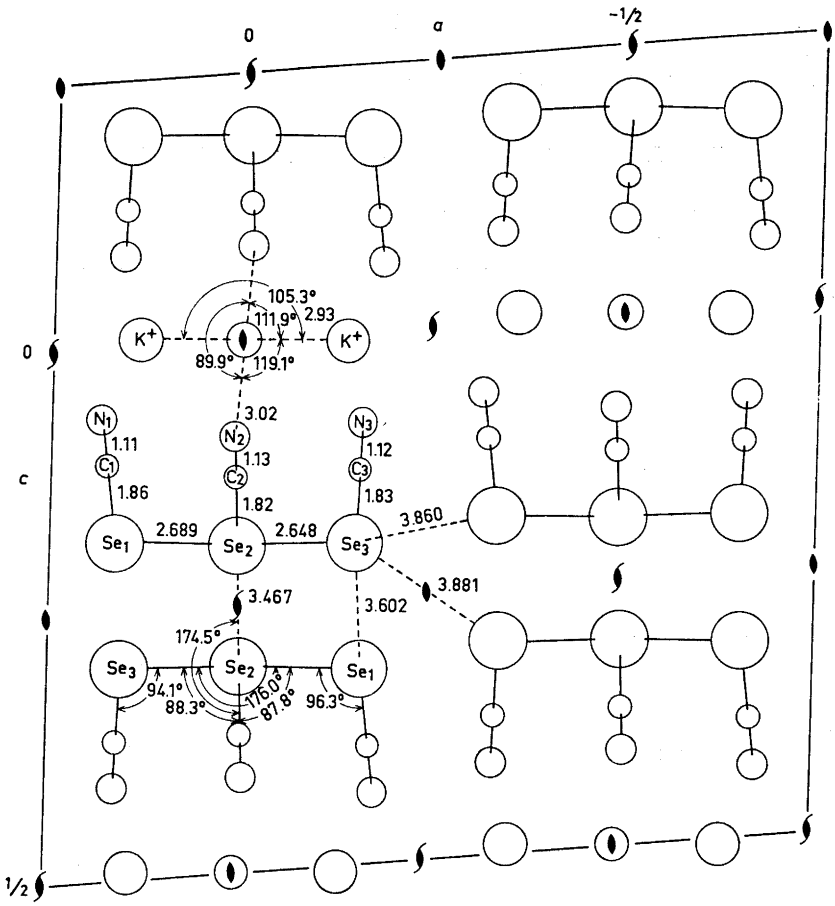

Fig. 1. Potassium triselenocyanate hemihydrate as seen along the *b* crystal axis.

Each of the three selenocyanate groups of the ion is linear within the error, the found values for the Se–C–N angles being 178–179° with rather large, about 2.5°, standard deviations. The Se–C bonds are 1.82–1.86 Å, each ±0.03 Å, and the C–N bonds, 1.11–1.13 Å, each ±0.04 Å.

In the selenocyanate ion in the crystals of potassium selenocyanate,[13] Se–C = 1.829(25) Å and C–N = 1.117(25) Å, ∠Se–C–N = 178.8(25)°. Thus, within the accuracy of the structure analyses, the process,

$$3\ SeCN^- = (SeCN)_3^- + 2\ e,$$

does not change the dimensions of the selenocyanate group.

The atoms of the terminal selenocyanate groups and the middle selenium atom, Se_2, are approximately co-planar, the largest deviation of an atom from

a least squares plane being 0.06 Å (*cf.* Table 6). So are the atoms of the middle selenocyanate group and the terminal selenium atoms, Se_1 and Se_3. These two planes make an angle of 57.4° with each other.

INTERIONIC SELENIUM – SELENIUM CONTACTS

There are in the crystals several close selenium-selenium contacts between adjacent triselenocyanate ions. The relevant data are listed in Table 5. In the table, a prime denotes an atom located at $(\bar{x},\frac{1}{2}+y,\frac{1}{2}-z)$ relative to the unprimed one, and a double-prime denotes an atom located at $(\bar{x},-\frac{1}{2}+y,\frac{1}{2}-z)$

Table 5. Close interionic selenium – selenium contacts. Bond lengths (Å) and angles (°). Standard deviations are given in parentheses.

$Se_2-Se_2' = 3.467(9)$	$\angle C_1-Se_1-Se_3' = 163.8(11)$
$Se_2-Se_2'' = 3.467(9)$	$\angle C_1-Se_1-Se_3'' = 118.6(11)$
$Se_1-Se_3' = 3.602(9)$	$\angle C_2-Se_2-Se_2' = 105.8(10)$
$Se_1-Se_3'' = 3.525(9)$	$\angle C_2-Se_2-Se_2'' = 174.5(10)$
	$\angle C_3-Se_3-Se_1' = 166.8(11)$
	$\angle C_3-Se_3-Se_1'' = 114.8(11)$

relative to the unprimed one; the primed and double-primed atoms are both related to the unprimed ones through the operation of the screw axis parallel to *b* near the middle selenium atom, Se_2.

Table 5 shows close $Se_2\cdots Se_2'$ and $Se_2\cdots Se_2''$ contacts of 3.467 Å, and close $Se_1\cdots Se_3'$ and $Se_1\cdots Se_3''$ contacts of 3.602 and 3.525 Å, respectively,

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 monoclinic axes, with coordinates X, Y, and Z in Å.

Plane through $Se_1C_1N_1$, Se_2, and $Se_3C_3N_3$:

$$0.0234\,X + 0.9162\,Y - 0.4003\,Z + 1.7829 = 0$$

Se_1	0.017 Å	C_1	0.018 Å	N_1	0.047 Å
Se_2	−0.058				
Se_3	0.043	C_3	−0.024	N_3	−0.052

Plane through Se_1, $Se_2C_2N_2$, and Se_3:

$$-0.0501\,X + 0.8309\,Y + 0.5564\,Z - 2.5446 = 0$$

Se_1	0.008 Å				
Se_2	−0.015	C_2	0.001 Å	N_2	0.003 Å
Se_3	0.008				

Plane through C_2, $Se_1Se_2Se_3$, and Se_2'':

$$-0.0553\,X + 0.7710\,Y + 0.6368\,Z - 2.8929 = 0$$

		Se_1	0.018 Å		
C_2	−0.161 Å	Se_2	0.004	Se_2''	−0.014 Å
		Se_3	0.019		

each ± 0.009 Å. For comparison, the Pauling [9] van der Waals radius of selenium is 2.00 Å.

One of these contacts, $Se_2\cdots Se_2'' = 3.467$ Å, is of particular interest. In the isolated triselenocyanate ion, the middle selenium atom, Se_2, is three-coordinated, being bonded at a $Se_1-Se_2-Se_3$ angle of 176.0° to two selenium atoms, Se_1 and Se_3, and, in a direction bisecting the $Se_1-Se_2-Se_3$ angle, to a carbon atom, C_2. The selenium atom Se_2'' lies approximately in the plane of $Se_1Se_2Se_3$ and C_2 (*cf.* Table 6), and the $C_2-Se_2\cdots Se_2''$ angle is 174.5°. The Se_2'' atom thus approaches the fourth coordination site of square-planar four-coordination at Se_2. This is a tendency encountered also in primarily three-coordinated complexes of tellurium(II).[11]

The $Se_2\cdots Se_2'$ contact, also 3.467 Å, occurs at a $C_2-Se_2\cdots Se_2'$ angle of 105.8°.

Each of the two terminal selenium atoms has, likewise, two close selenium neighbours, at 3.602 Å and 3.525 Å, $Se_1\cdots Se_3'$ being equal to $Se_3\cdots Se_1''$, and $Se_1\cdots Se_3''$ being equal to $Se_3\cdots Se_1'$. These contacts occur at $C-Se\cdots Se$ angles of 163.8° and 118.6° at Se_1, and 166.8° and 114.8° at Se_3.

THE ENVIRONMENT OF THE POTASSIUM ION AND THE WATER MOLECULE

The water molecule lies on the twofold axis at (0,*y*,0). It is surrounded by two potassium ions at distances of 2.93(3) Å and a $K\cdots O\cdots K$ angle of 105.3(10)°, and by two N_2 nitrogen atoms at distances of 3.02(5) Å and a $N\cdots O\cdots N$ angle of 89.9(12)°. The latter contacts probably involve weak $O-H\cdots H$ hydrogen bonds. The arrangement around the water molecule is approximately tetrahedral, the $K\cdots O\cdots N$ angles being 119.1(7)° and 111.9(8)°.

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

$K\cdots N_1(\bar{x},y,\bar{z})$	= 2.98 Å	$K\cdots N_3(x,y,z)$	= 2.96 Å
$K\cdots N_1(\bar{x},1+y,\bar{z})$	= 2.95	$K\cdots N_3(x,1+y,z)$	= 2.86
$K\cdots N_1(\frac{1}{2}+x,\frac{1}{2}+y,z)$	= 3.20	$K\cdots O$	= 2.93
$K\cdots N_2(\bar{x},y,\bar{z})$	= 3.04		

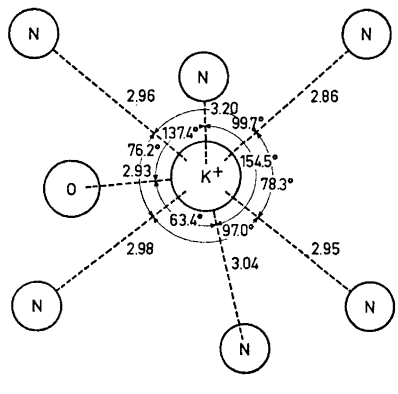

Fig. 2. The surroundings of the potassium ion in potassium triselenocyanate hemihydrate, as seen along the *a* crystal axis.

The closest contacts of the potassium ion are listed in Table 7 and shown in Fig. 2. The potassium ion is surrounded by five nitrogen atoms, at distances ranging from 2.86 to 3.04 Å, and by one oxygen atom, at 2.93 Å. The shape of the resulting polyhedron is rather irregular. Four of the five nitrogen atoms, at K···N = 2.86 to 2.98 Å, lie exactly in a plane; the potassium ion lies 0.57 Å from this plane. The K···O distance is in the normal range (*cf.* Ref. 8, p. 258) and so are the K···N distances: the sum of the K···N ionic radii is 3.04 Å;[9] in potassium selenocyanate,[13] the closest K···N distances are 2.89, 2.94, and 3.12 Å, and in potassium thiocyanate,[14] 2.97 and 2.98 Å.

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