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The Crystal Structure of Cesium Triselenocyanate

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The crystal structure of cesium triselenocyanate, $Cs(SeCN)_3$, has been determined by X-ray methods, and refined by full-matrix least squares procedures. The crystals are monoclinic, space group $C2/c$ (No. 15). with $a=7.969(4)$ Å, $b=21.156(10)$ Å, $c=5.593(4)$ Å, and $\beta=98.84(6)°$, and four formula units per unit cell.

The triselenocyanate ion possesses by space group requirements a twofold axis of symmetry; the middle selenocyanate group is located on this axis. The three-selenium sequence of the triselenocyanate ion is very nearly linear, with Se—Se—Se bond angle 178.31(10)°, and Se—Se bond lengths of 2.650(3) Å, which is 0.31 Å longer than single covalent selenium-selenium bonds.

The middle selenocyanate group, located on a twofold axis, is exactly linear, and the terminal selenocyanate groups are linear within error. A least squares plane through a terminal selenocyanate group and the middle selenium atom makes an angle of 43.9° with the plane through the middle selenocyanate group and the terminal selenium atoms.

Cesium triselenocyanate, $Cs(SeCN)_3$, was first prepared in 1925 by Birckenback and Kellermann.[1]

The crystal structures of the triselenocyanate ion in the potassium and rubidium salts, both hemihydrates, have been determined.[2,3] In the potassium salt, no molecular symmetry is required. In the rubidium salt, the triselenocyanate ion lies across a crystallographic mirror plane, with the middle selenocyanate group in the plane. In the cesium salt, the present work, the middle selenocyanate group is located on a crystallographic twofold axis.

CRYSTAL DATA

Preparative and crystallographic data, and a short note of the crystal structure of cesium triselenocyanate have been reported earlier.[4,5]

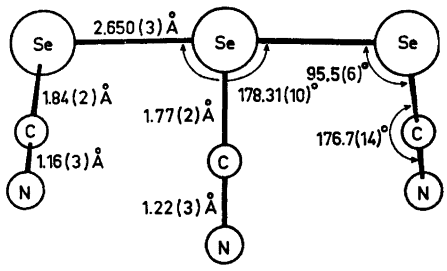

Fig. 1. The triselenocyanate ion in $Cs(SeCN)_3$, as seen normal to the plane through the middle selenocyanate group and the terminal selenium atoms.

The salt, $Cs(SeCN)_3$, forms brown monoclinic prisms extended along the c axis, with $a=7.969(4)$ Å, $b=21.156(10)$ Å, $c=5.593(4)$ Å, and $\beta=98.84(6)°$. The unit cell dimensions were determined from zero-layer Weissenberg photographs around the three axis; 32 observations were measured and evaluated by means of a least squares program.

There are four formula units per unit cell; density, calc. and found 3.18 g/cm³. The space group, from systematic absences and subsequent structure analysis, is $C2/c$ (No. 15).

Intensities were estimated visually from integrated Weissenberg photographs around the a and c axes, taken with Cu$K\alpha$ radiation using the multi-film technique. The three-dimensional refinement was based on the $0kl-2kl$ and $hk0-hk3$ data. In all 637 out of 842 independent reflections accessible with Cu$K\alpha$ radiation were observed with measurable intensities. Three different crystals were used; the crystal used for collection of $0kl-2kl$ data had the following dimensions, from an arbitrarily chosen origin to crystal faces: to (010) and $(0\bar{1}0)$, 0.037 mm; to $(2\bar{1}0)$ and $(\bar{2}10)$, 0.058 mm; to $(01\bar{2})$ and $(0\bar{1}2)$, 0.070 mm. The dimensions of the crystal used for $hk0-hk2$ data were: to $(\bar{1}00)$ and (100), 0.025 mm; to $(0\bar{1}0)$ and (010), 0.040 mm; to $(\bar{1}2\bar{1})$ and $(12\bar{1})$, 0.070 mm. The dimensions of the crystal used for $hk3$ data were:

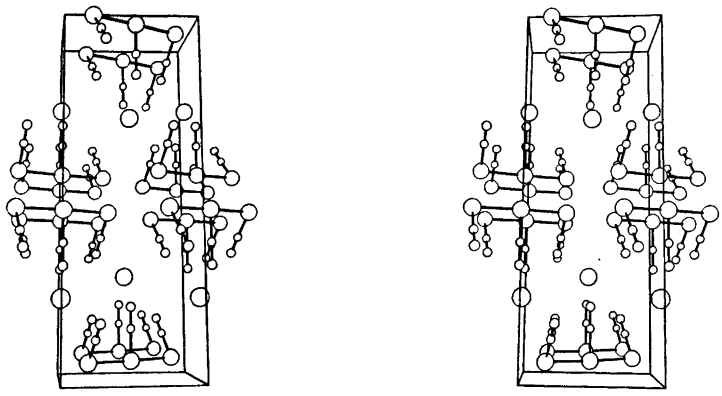

Fig. 2. A stereoscopic pair of drawings showing the content of the unit cell.

to (010) and (0$\bar{1}$0), 0.019 mm; to (110) and ($\bar{1}$10), 0.023 mm; to (12$\bar{1}$) and ($\bar{1}\bar{2}$1), 0.043 mm. The linear absorption coefficient, μ=456.8 cm^{-1}.

The intensities were corrected for absorption by the method of Coppens *et al.*[6] The subdivisions in Gaussian points along the *a*, *b*, and *c* axes were, respectively: for the crystal used for collection of $0kl-2kl$ data, 10, 6, and 10; for the crystal used for collection of $hk0-hk2$ data, 8, 10, and 8; and for the crystal used for collection of $hk3$ data, 8, 8, and 10.

Later the structure factors were corrected for secondary extinction, using the method of Zachariasen,[7] neglecting the absorption term: $F_{corr}=KF_o(1+\beta CI_o)$, where $\beta=2(1+\cos^4 2\theta)/(1+\cos^2 2\theta)^2$. C was found to be 3.2×10^{-6}, 3.3×10^{-6}, and 2.5×10^{-6}, for the $0kl-2kl$, $hk0-hk2$, and $hk3$ data, respectively. The intensities of reflections that occurred more than once in the data set were then averaged, and such reflections thereafter included only once.

THE STRUCTURE ANALYSIS

With four cesium ions and four triselenocyanate ions in the unit cell, the space group, $C2/c$, if correct, would demand that the ions lie in special positions. From the $hk0$ and $0kl$ Patterson maps it was found that both the cesium ion and the middle selenocyanate group in the triselenocyanate ion were located on a crystallographic twofold axis.

The approximate y coordinate of the cesium ion was found from the $hk0$ and $0kl$ Patterson maps. The selenium atoms were placed partly on the basis of subsequent $hk0$ and $0kl$ Fourier maps and partly on the basis of the two Patterson maps. The positions of the carbon and nitrogen atoms were found from a three-dimensional Fourier map based on the determined positions of the cesium and selenium atoms, and from known dimensions of the triselenocyanate group.

The three-dimensional refinement was carried out on the IBM 360/50H computer using a full-matrix least squares program minimizing the function

$$r = \sum W(|F_o|-K|F_c|),^2$$

where K is the scale factor and

$$W=1/[(Ka_1)^2+(a_2F_o)^2/4W_o+(a_3F_o)].$$

The weight W_o is based on the estimated reliability of the film readings. The constant a_1, a_2, and a_3 were given the values 0.8, 0.15, and 0.004, respectively. Unobserved reflections with calculated structure factors, $|F_c|$, greater than threshold value, F_t, were included in the refinement with F_o equal to F_t.

The final refinement, with anisotropic temperature factors for all atoms, brought the reliability index, R, down to 0.062, with unobserved reflections included if $|F_c|$ exceeds the observable limit, F_t.

A three-dimensional Fourier difference map based on the data of Table 3 showed no higher peak than 1.4 e Å^{-3}.

Most computer programs 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 programs used for secondary extinction corrections and Fourier summations were written by K. Åse, and the programs used for calculating distances and angles, and least squares planes, were written by K. Maartmann-Moe, both of this Institute.

Table 1. Atomic coordinates for cesium triselenocyanate in fractions of monoclinic cell edges, with origin on a center of symmetry. Standard deviations from least squares are given in parentheses.

	x	y	z
Cs	0	0.22063(7)	1/4
Se_1	0.1850(3)	0.05816(8)	0.0356(4)
Se_2	½	0.05631(10)	1/4
C_1	0.222(3)	0.1196(8)	−0.185(3)
C_2	½	0.1400(11)	1/4
N_1	0.246(3)	0.1603(9)	−0.314(4)
N_2	½	0.1978(9)	1/4

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

	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Cs	5.68(12)	3.44(5)	3.32(6)	0	−0.95(7)	0
Se_1	3.39(9)	3.84(7)	5.42(10)	0.31(6)	−0.32(8)	−0.24(7)
Se_2	3.77(13)	2.57(8)	4.29(11)	0	−0.48(11)	0
C_1	3.8(8)	5.0(8)	3.8(7)	−0.1(6)	−1.5(8)	−0.5(7)
C_2	10.9(26)	3.4(9)	4.7(12)	0	0.0(16)	0
N_1	6.1(12)	6.9(9)	8.3(12)	1.9(9)	−0.7(11)	1.5(10)
N_2	8.3(18)	2.5(7)	6.1(12)	0	2.1(13)	0

The calculated structure factors were based on atomic scattering factors given in *International Tables* (Ref. 8, Table 3.3.1A). The scattering factors for cesium and selenium 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 factors are listed in Tables 1 and 2, and structure factors in Table 3.

RESULTS

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 Tables 4 and 5 a prime denotes an atom located at $1-x,y,\frac{1}{2}-z$ relative to the unprimed one.

In the triselenocyanate ion, the symmetry of a twofold axis makes the two Se—Se bonds equal. The Se—Se bond length is 2.650(3) Å. The three-selenium sequence is very nearly linear, with Se—Se—Se bond angle of 178.31(10)°. The middle selenocyanate group, located on a twofold axis, is exactly linear and bisects the Se—Se—Se angle. The terminal selenocyanate group is linear within error; the Se—C—N angle is 176.7(14)°. The Se—Se—C bond angle is 89.15(7)° at the central selenium atom, and 95.5(6)° at the terminal selenium atom.

Due to the twofold axis, the atoms of the middle selenocyanate group and the terminal selenium atoms of the three-selenium sequence are exactly coplanar. The atoms of a terminal selenocyanate group and the central selenium atom are approximately coplanar, the largest deviation of an atom from a least squares plane being 0.03 Å. The angle between the two least squares planes is 87.8°, and the angle between one of the least squares planes, and the plane through the middle selenocyanate group and the two terminal selenium atoms, is one half of this value, 43.9°.

This is the third crystal structure reported of a salt of the triselenocyanate ion. The triseleno-

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)
0	2	0	45	49
0	4	0	113	107
0	6	0	206	-211
0	8	0	241	-244
0	10	0	187	-184
0	12	0	166	-157
0	14	0	148	148
0	16	0	56	50
0	18	0	177	183
0	20	0	15	13
0	22	0	19	16
0	24	0	54	-52
0	26	0	45	-46
0	2	1	142	-140
0	4	1	36	-31
0	6	1	288	-305
0	8	1	131	131
0	10	1	78	-77
0	12	1	176	178
0	14	1	42	40
0	16	1	38	35
0	18	1	-10	6
0	20	1	60	-56
0	22	1	12	-12
0	24	1	60	-58
0	26	1	26	25
0	0	2	161	-162
0	2	2	218	220
0	4	2	80	-74
0	6	2	-8	3
0	8	2	70	-65
0	10	2	67	-64
0	12	2	63	61
0	14	2	55	-53
0	16	2	88	88
0	18	2	45	-42
0	20	2	43	39
0	22	2	32	-28
0	24	2	-7	1
0	26	2	-4	-1
0	2	3	40	33
0	4	3	94	-94
0	6	3	105	101
0	8	3	91	-95
0	10	3	95	93
0	12	3	62	-60
0	14	3	30	26
0	16	3	12	-11
0	18	3	24	-19
0	20	3	21	15
0	22	3	19	-17
0	24	3	40	32
0	0	4	171	155
0	2	4	20	-16
0	4	4	70	75
0	6	4	76	-79
0	8	4	75	-72
0	10	4	47	-47
0	12	4	61	-66
0	14	4	58	61
0	16	4	-10	-2
0	18	4	81	74
0	20	4	9	-3
0	22	4	16	16
0	2	5	79	-78
0	4	5	26	-25
0	6	5	91	-101
0	8	5	33	37
0	10	5	24	-24
0	12	5	80	80
0	14	5	25	23
0	16	5	21	21
0	18	5	-6	-2
0	0	6	52	-52
0	2	6	28	31
0	4	6	31	-33
0	6	6	23	22
0	8	6	-10	9
0	10	6	-9	0
0	12	6	19	20
0	14	6	23	-26
0	2	7	10	12
0	4	7	15	-20
1	3	0	87	-86
1	5	0	113	120
1	7	0	130	-137
1	9	0	164	164
1	11	0	87	-88
1	13	0	82	86
1	15	0	49	-48
1	17	0	-10	-8
1	19	0	-10	5
1	21	0	49	-49
1	23	0	42	36
1	25	0	25	-23
1	27	0	21	24
1	1	1	101	-101
1	3	1	59	56
1	5	1	206	-215
1	7	1	29	24
1	9	1	36	32
1	11	1	-11	-4
1	13	1	112	114
1	15	1	55	-53
1	17	1	67	68
1	19	1	81	-83
1	21	1	26	22
1	23	1	23	-21
1	25	1	-7	6
1	1	2	68	61
1	3	2	112	109
1	5	2	130	-132
1	7	2	67	66
1	9	2	154	-163
1	11	2	47	44
1	13	2	83	-84
1	15	2	63	63
1	17	2	42	36
1	19	2	-11	6
1	21	2	47	44
1	23	2	37	-37
1	25	2	14	13
1	1	3	39	40
1	3	3	246	-248
1	5	3	84	-86
1	7	3	137	-139
1	9	3	-12	7
1	11	3	147	141
1	13	3	65	57
1	15	3	121	122
1	17	3	46	-41
1	19	3	16	14
1	21	3	85	-79
1	23	3	31	-27
1	1	4	69	-68
1	3	4	76	-77
1	5	4	85	93
1	7	4	22	-18
1	9	4	113	125
1	11	4	20	-14
1	13	4	49	47
1	15	4	56	-55
1	17	4	45	-39
1	19	4	15	-12
1	21	4	29	-27
1	1	5	55	-63
1	3	5	44	43
1	5	5	44	-42
1	7	5	25	21
1	9	5	-12	5
1	11	5	28	-23
1	13	5	37	32
1	15	5	31	-30
1	17	5	32	29
1	1	6	-12	-6
1	3	6	19	18
1	5	6	31	-33
1	7	6	41	41
1	9	6	31	-31
1	11	6	25	25
1	13	6	24	-24
1	1	-1	48	42
1	3	-1	449	-411
1	5	-1	145	-141
1	7	-1	167	-170
1	9	-1	-12	10
1	11	-1	151	161
1	13	-1	94	94
1	15	-1	172	184
1	17	-1	61	-61
1	19	-1	17	13
1	21	-1	94	-104
1	23	-1	44	-35
1	25	-1	23	-21
1	1	-2	179	186
1	3	-2	164	148
1	5	-2	138	-129
1	7	-2	39	-26
1	9	-2	299	-294
1	11	-2	-21	-5
1	13	-2	50	-51
1	15	-2	96	101
1	17	-2	76	76
1	19	-2	45	44
1	21	-2	53	49
1	23	-2	60	-53
1	1	-3	93	-98
1	3	-3	109	111
1	5	-3	64	-60
1	7	-3	23	22
1	9	-3	-13	9
1	11	-3	27	-23
1	13	-3	40	33
1	15	-3	68	-70
1	17	-3	56	55
1	19	-3	41	-38
1	21	-3	34	32
1	23	-3	-7	-6
1	1	-4	44	42
1	3	-4	22	-23
1	5	-4	44	41
1	7	-4	94	-93
1	9	-4	57	55
1	11	-4	62	-63
1	13	-4	34	36
1	15	-4	-13	-6
1	17	-4	20	16
1	19	-4	13	13
1	21	-4	27	-25
1	3	-5	43	41
1	5	-5	74	-77
1	7	-5	-13	7
1	9	-5	31	-29
1	11	-5	-13	-7
1	13	-5	28	27
1	15	-5	-13	-3
1	17	-5	48	49
1	19	-5	26	-24
1	21	-5	18	19
1	1	-6	38	32
1	3	-6	35	36
1	5	-6	36	-34
1	7	-6	-12	3
1	9	-6	64	-65
1	11	-6	-10	5
1	13	-6	15	-17
1	1	-7	14	-17
1	3	-7	28	32
2	2	0	193	-194
2	4	0	154	164
2	6	0	52	-56
2	8	0	31	23
2	10	0	63	61
2	12	0	74	-74
2	14	0	74	72
2	16	0	80	-80
2	18	0	47	43
2	20	0	35	-31
2	22	0	40	35
2	24	0	-9	-10
2	26	0	-6	-6
2	2	1	284	-277
2	4	1	58	-54
2	6	1	240	-258
2	8	1	77	73
2	10	1	55	-53
2	12	1	160	147
2	14	1	67	66
2	16	1	59	59
2	18	1	-11	-4
2	20	1	77	-76
2	22	1	28	-19
2	24	1	54	-55
2	26	1	14	19
2	0	2	322	-356
2	2	2	43	-35
2	4	2	148	-146
2	6	2	159	171
2	8	2	171	178
2	10	2	116	115
2	12	2	108	110
2	14	2	111	-116
2	16	2	34	-27
2	18	2	119	-127
2	20	2	14	-10
2	22	2	22	-20
2	24	2	37	43
2	2	3	96	91
2	4	3	47	-39
2	6	3	119	120
2	8	3	84	-80
2	10	3	77	71
2	12	3	88	-86
2	14	3	-14	0
2	16	3	25	-23
2	18	3	-12	-4
2	20	3	39	33
2	22	3	11	-9
2	0	4	61	59
2	2	4	98	-103
2	4	4	55	58
2	6	4	-12	-14
2	8	4	31	30
2	10	4	37	32
2	12	4	39	-34
2	14	4	43	37
2	16	4	62	-55
2	18	4	31	26
2	20	4	23	-22
2	2	5	31	-32
2	4	5	29	27
2	6	5	64	-64
2	8	5	47	45
2	10	5	42	-43
2	12	5	45	43
2	14	5	-10	-6
2	16	5	12	12
2	0	6	86	-84
2	2	6	17	11
2	4	6	32	-30
2	6	6	34	34
2	8	6	27	25
2	10	6	23	18
2	12	6	30	30
2	2	-1	83	84
2	4	-1	199	-211
2	6	-1	66	65
2	8	-1	104	-113
2	10	-1	132	141
2	12	-1	46	-41
2	14	-1	62	60
2	16	-1	13	-10
2	18	-1	31	-26
2	20	-1	17	11
2	22	-1	39	-34
2	24	-1	32	28
2	26	-1	16	-15
2	0	-2	238	-263
2	2	-2	40	33
2	4	-2	126	-125
2	6	-2	123	115
2	8	-2	105	95
2	10	-2	58	52
2	12	-2	101	97
2	14	-2	83	-84
2	16	-2	-12	6
2	18	-2	92	-91
2	20	-2	-12	0
2	22	-2	28	-25
2	24	-2	31	26
2	2	-3	171	-165
2	4	-3	87	-83
2	6	-3	206	-212
2	8	-3	50	46
2	10	-3	22	-14
2	12	-3	151	156
2	14	-3	63	63
2	16	-3	45	44
2	18	-3	-12	-5
2	20	-3	63	-60
2	22	-3	29	-24
2	24	-3	35	-44
2	0	-4	135	138
2	2	-4	39	-35
2	4	-4	55	52
2	6	-4	59	-54
2	8	-4	40	-35
2	10	-4	24	-18
2	12	-4	45	-47
2	14	-4	52	51
2	16	-4	-13	-10
2	18	-4	52	49
2	20	-4	12	-10
2	22	-4	9	10
2	2	-5	-14	8
2	4	-5	53	-49
2	6	-5	39	37
2	8	-5	43	-44
2	10	-5	39	41
2	12	-5	20	-21
2	14	-5	21	20
2	16	-5	-10	-2
2	18	-5	9	-8
2	0	-6	46	-42
2	2	-6	34	29
2	4	-6	22	-21
2	6	-6	-13	12
2	8	-6	-13	-3
2	10	-6	-12	-4
2	12	-6	19	20
2	14	-6	16	-16
2	2	-7	15	-17
2	4	-7	-7	-1
3	0	0	104	96
3	1	0	224	-244
3	3	0	168	-164
3	5	0	165	161
3	7	0	67	59
3	9	0	283	296
3	11	0	43	37
3	13	0	67	64
3	15	0	119	-117
3	17	0	102	-101
3	19	0	49	-54
3	21	0	43	-47
3	23	0	44	54
3	25	0	15	13
4	0	0	197	226
4	2	0	71	-69
4	4	0	64	63
4	6	0	61	-55
4	8	0	45	-39
4	10	0	33	-28
4	12	0	76	-70
4	14	0	61	58
4	16	0	25	-23
4	18	0	71	73
4	20	0	-20	-9
4	22	0	19	18
4	24	0	13	-14
5	1	0	64	67
5	3	0	26	-22
5	5	0	44	36
5	7	0	105	-98
5	9	0	42	34
5	11	0	78	-73
5	13	0	44	39
5	15	0	-24	-1
5	17	0	27	20
5	19	0	24	18
5	21	0	17	-22
5	23	0	12	13
6	0	0	171	171
6	2	0	37	35
6	4	0	62	64
6	6	0	85	-90
6	8	0	95	-96
6	10	0	64	-64
6	12	0	56	-55
6	14	0	59	57
6	16	0	27	25
6	18	0	59	64
6	20	0	-13	7
6	22	0	7	8
7	1	0	59	-50
7	3	0	38	-40
7	5	0	44	44
7	7	0	-21	0
7	9	0	70	73
7	11	0	-20	7
7	13	0	31	26
7	15	0	26	-26
7	17	0	24	-26
7	19	0	12	-15
8	0	0	-19	2
8	2	0	49	-48
8	4	0	-19	14
8	6	0	-18	6
8	8	0	29	25
8	10	0	25	22
8	12	0	-15	-7
8	14	0	-12	5
8	16	0	22	-26
9	1	0	32	-29
9	3	0	28	-27
9	5	0	22	16
9	7	0	19	16
9	9	0	43	46
9	11	0	-10	5
10	0	0	35	37
10	2	0	12	12
10	4	0	-8	11
3	1	1	71	-68
3	3	1	264	259
3	5	1	96	87
3	7	1	126	122
3	9	1	-25	-11
3	11	1	128	-119
3	13	1	57	-50
3	15	1	138	-135
3	17	1	51	49
3	19	1	-28	-18
3	21	1	68	77
3	23	1	25	25
3	25	1	-13	17
4	2	1	33	29
4	4	1	146	134
4	6	1	66	-56
4	8	1	107	102
4	10	1	102	-104
4	12	1	-30	18
4	14	1	63	-56
4	16	1	-30	-4
4	18	1	-28	23
4	20	1	-25	3
4	22	1	28	27
4	24	1	17	-24
5	1	1	34	-36
5	3	1	145	147
5	5	1	-26	20
5	7	1	73	63
5	9	1	-29	3
5	11	1	75	-69
5	13	1	-31	-20
5	15	1	83	-77

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)
5	17	1	35	32	5	21	-1	-18	-17	5	21	2	24	30	6	4	-2	-29	-31	6	16	3	-10	-6
5	19	1	-22	-13	5	23	-1	-12	6	6	0	2	53	-53	6	6	-2	-30	-1	7	1	3	-17	16
5	21	1	39	47	6	2	-1	40	31	6	2	2	55	46	6	8	-2	-30	-33	7	3	3	64	-72
5	23	1	10	10	6	4	-1	46	-41	6	4	2	51	-52	6	10	-2	-31	-33	7	5	3	25	-26
6	2	1	109	-114	6	6	-1	47	45	6	6	2	-31	24	6	12	-2	-30	20	7	7	3	28	-33
6	4	1	65	-66	6	8	-1	39	-40	6	8	2	-31	7	6	14	-2	-29	-12	7	9	3	-14	5
6	6	1	128	-130	6	10	-1	37	36	6	10	2	-31	-3	6	16	-2	36	34	7	11	3	37	36
6	8	1	-27	22	6	12	-1	34	-33	6	12	2	34	28	6	18	-2	-21	-7	7	13	3	19	16
6	10	1	-27	-7	6	14	-1	-26	13	6	14	2	38	-31	6	20	-2	-16	14	8	1	-3	68	-67
6	12	1	103	103	6	16	-1	-23	-7	6	16	2	30	27	7	1	-2	36	31	8	3	-3	79	79
6	14	1	48	48	6	18	-1	-20	-6	6	18	2	25	-26	7	3	-2	29	29	8	5	-3	40	-33
6	16	1	36	37	6	20	-1	-16	13	7	1	2	-28	-12	7	5	-2	40	-34	8	7	-3	52	52
6	18	1	-19	-5	7	1	-1	-25	1	7	3	2	-28	10	7	7	-2	-28	-1	8	9	-3	-15	9
6	20	1	40	-44	7	3	-1	108	-112	7	5	2	37	-27	7	9	-2	52	-49	8	11	-3	42	-40
7	1	1	59	-55	7	5	-1	74	-72	7	7	2	52	45	7	11	-2	-27	2	8	13	-3	24	22
7	3	1	-25	4	7	7	-1	68	-65	7	9	2	32	-26	7	13	-2	-25	-16	8	15	-3	31	-33
7	5	1	44	-43	7	9	-1	-25	10	7	11	2	33	26	7	15	-2	-21	24	8	17	-3	30	24
7	7	1	-25	3	7	11	-1	67	68	7	13	2	-22	-20	7	17	-2	-17	18	8	19	-3	34	-35
7	9	1	-24	5	7	13	-1	52	45	7	15	2	-18	5	7	19	-2	-10	7	8	21	-3	28	30
7	11	1	-23	2	7	15	-1	53	58	7	17	2	-11	-2	8	0	-2	79	-76	8	23	-3	-8	8
7	13	1	32	35	7	17	-1	-16	-11	8	0	2	103	-98	8	2	-2	-26	-21	4	2	-3	24	-17
7	15	1	-18	-15	7	19	-1	-12	-5	8	2	2	25	-22	8	4	-2	26	-22	4	4	-3	64	64
7	17	1	18	17	8	2	-1	-23	11	8	4	2	23	-21	8	6	-2	31	33	4	6	-3	43	-42
8	2	1	28	-28	8	4	-1	-23	-9	8	6	2	45	43	8	8	-2	51	45	4	8	-3	61	61
8	4	1	-22	-1	8	6	-1	27	26	8	8	2	48	48	8	10	-2	34	35	4	10	-3	59	-59
8	6	1	43	-40	8	8	-1	-21	-17	8	10	2	38	37	8	12	-2	28	22	4	12	-3	26	24
8	8	1	-20	20	8	10	-1	-20	21	8	12	2	27	29	8	14	-2	23	-20	4	14	-3	25	-21
8	10	1	-19	-13	8	12	-1	-18	-15	9	1	2	-16	6	9	1	-2	-21	-14	4	16	-3	-16	2
8	12	1	30	29	8	14	-1	-15	-1	9	3	2	-16	18	9	3	-2	-20	2	4	18	-3	-14	7
8	14	1	-13	4	9	1	-1	-19	16	9	5	2	-14	-12	9	5	-2	-19	-3	4	20	-3	-12	-8
9	1	1	-17	6	9	3	-1	-18	-5	9	7	2	-12	4	9	7	-2	-18	19	4	22	-3	-8	14
9	3	1	65	63	9	5	-1	22	19	1	25	-2	-18	-8	9	9	-2	-16	-3	5	1	-3	-16	-9
9	5	1	34	35	9	7	-1	-17	3	3	1	-2	72	-70	9	11	-2	-13	12	5	3	-3	134	130
9	7	1	27	29	9	9	-1	-15	-3	3	3	-2	-24	16	10	2	-2	-11	3	5	5	-3	66	61
9	9	1	-13	-1	9	11	-1	-13	-3	3	5	-2	71	-69	3	1	3	103	104	5	7	-3	96	96
9	11	1	26	-32	10	2	-1	27	25	3	7	-2	134	138	3	3	3	61	-59	5	9	-3	-17	-8
3	1	-1	65	94	10	4	-1	25	26	3	9	-2	-27	-22	3	5	3	84	81	5	11	-3	62	-61
3	3	-1	146	-149	3	1	2	37	-36	3	11	-2	84	85	3	7	3	-17	-5	5	13	-3	42	-43
3	5	-1	20	21	3	3	2	36	32	3	13	-2	72	-65	3	9	3	-18	-15	5	15	-3	61	-58
3	7	-1	85	-85	3	5	2	69	-69	3	15	-2	-32	7	3	11	3	-19	1	5	17	-3	22	21
3	9	-1	-23	3	3	7	2	128	126	3	17	-2	-31	-21	3	13	3	55	-54	5	19	-3	-11	2
3	11	-1	76	77	3	9	2	89	-88	3	19	-2	-30	-26	3	15	3	54	51	5	21	-3	33	42
3	13	-1	-27	-14	3	11	2	77	76	3	21	-2	-26	26	3	17	3	47	-45	6	2	-3	37	-34
3	15	-1	76	82	3	13	2	59	-51	3	23	-2	-21	-16	3	19	3	42	44	6	4	-3	-17	0
3	17	-1	57	-51	3	15	2	-36	16	3	25	-2	28	28	3	21	3	19	-18	6	6	-3	56	-56
3	19	-1	43	37	3	17	2	-35	-12	4	0	-2	196	-225	4	2	3	105	100	6	8	-3	20	18
3	21	-1	41	-50	3	19	2	-32	-12	4	2	-2	-26	5	4	4	3	62	58	6	10	-3	18	-17
3	23	-1	-21	-6	3	21	2	-27	32	4	4	-2	64	-66	4	6	3	172	163	6	12	-3	38	37
3	25	-1	-15	-9	3	23	2	32	-23	4	6	-2	74	83	4	8	3	48	-42	6	14	-3	-14	8
4	2	-1	151	160	4	0	2	131	-146	4	8	-2	86	90	4	10	3	-19	17	6	16	-3	-12	14
4	4	-1	138	129	4	2	2	77	85	4	10	-2	65	59	4	12	3	115	-122	6	18	-3	-10	0
4	6	-1	236	246	4	4	2	60	-55	4	12	-2	69	60	4	14	3	38	-38	7	1	-3	30	-26
4	8	-1	55	-51	4	6	2	45	38	4	14	-2	68	-68	4	16	3	32	-31	7	3	-3	-17	1
4	10	-1	-26	8	4	8	2	-36	0	4	16	-2	-32	-9	4	18	3	-14	-1	7	5	-3	32	-31
4	12	-1	170	-172	4	10	2	-37	-6	4	18	-2	72	-77	4	20	3	38	44	7	7	-3	-16	1
4	14	-1	88	-84	4	12	2	58	55	4	20	-2	-26	0	5	1	3	38	40	7	9	-3	-15	3
4	16	-1	45	-49	4	14	2	45	-45	4	22	-2	-21	-9	5	3	3	99	-98	7	11	-3	-14	1
4	18	-1	-27	8	4	16	2	49	34	4	24	-2	21	24	5	5	3	-18	-8	7	13	-3	20	21
4	20	-1	58	64	4	18	2	59	-53	5	1	-2	78	86	5	7	3	52	-50	7	15	-3	-11	-6
4	22	-1	32	33	4	20	2	-26	20	5	3	-2	75	76	5	9	3	-18	-3	7	17	-3	13	11
4	24	-1	35	50	4	22	2	-19	-17	5	5	-2	58	-56	5	11	3	54	54	8	2	-3	36	-32
5	1	-1	66	70	5	1	2	112	121	5	7	-2	-31	-21	5	13	3	-17	5	8	4	-3	30	-26
5	3	-1	54	-53	5	3	2	116	109	5	9	-2	148	-141	5	15	3	52	55	8	6	-3	36	-39
5	5	-1	66	63	5	5	2	95	-87	5	11	-2	-33	-10	5	17	3	23	-25	8	8	-3	-13	7
5	7	-1	-26	-9	5	7	2	51	-46	5	13	-2	-33	-29	5	19	3	14	16	8	10	-3	-12	1
5	9	-1	-26	-16	5	9	2	172	-171	5	15	-2	51	46	6	2	3	-18	9	8	12	-3	29	32
5	11	-1	-29	1	5	11	2	-35	-20	5	17	-2	46	41	6	4	3	59	-58	8	14	-3	17	18
5	13	-1	38	-35	5	13	2	46	-38	5	19	-2	35	27	6	6	3	22	16	9	1	-3	-12	-2
5	15	-1	50	44	5	15	2	74	69	5	21	-2	26	28	6	8	3	43	-44	9	3	-3	22	23
5	17	-1	-27	-30	5	17	2	62	64	6	0	-2	-29	-10	6	10	3	48	52	9	5	-3	13	12
5	19	-1	35	34	5	19	2	37	33	6	2	-2	69	69	6	12	3	-15	-9	9	7	-3	15	12
															6	14	3	18	22	9	9	-3	-7	0

cyanate ion has in all three salts been found to have a nearly linear three-selenium sequence. In the potassium salt [2] no molecular symmetry is required, and the three-selenium sequence is asymmetric with Se—Se bonds of 2.689(4) Å and 2.648(4) Å. In the rubidium salt [3] the three-selenium sequence is symmetric and the Se—Se bond length is 2.656(3) Å, which is within the error equal to the Se—Se bond length in the present structure.

In the crystal structures of salts of the triiodide ion the total length of the three-center system increases with increasing asymmetry.[9] The same trend is found in the structures of the triselenocyanate ion.

In the potassium and rubidium salts of the triselenocyanate ion, the terminal selenocyanate groups and the central selenium atom are approximately coplanar. In the present structure, the cesium salt, the triselenocyanate ion is fanshaped.

In the middle selenocyanate group the Se—C bond length is 1.77(2) Å and the C—N bond length is 1.22(3) Å. In the terminal group the lengths are 1.84(2) and 1.16(3) Å, respectively. Within the accuracy of the analysis these values

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

Se_1-Se_2	2.650(3)	$\angle Se_1-Se_2-Se_1'$	178.31(10)
Se_1-C_1	1.84(2)	$\angle Se_1-C_1-N_1$	176.7(14)
Se_2-C_2	1.77(2)	$\angle Se_2-C_2-N_2$	180
C_1-N_1	1.16(3)	$\angle Se_1-Se_2-C_2$	89.15(7)
C_2-N_2	1.22(3)	$\angle Se_2-Se_1-C_1$	95.5(6)

Table 5. Equations of planes and distances (Å) from least squares planes. The equations of the least squares planes were calculated with the selenium coordinates given six times the weight of the carbon and nitrogen coordinates. The equations refer to the axes of the unit cell, with coordinates X, Y, and Z in Å.

Plane through Se_1, Se_2 C_2 N_2, and Se_1'
$-0.44937\ X+0.94048\ Z+0.47536=0$
The atoms are exactly coplanar.

Plane through Se_1 C_1 N_1 and Se_2
$-0.31512\ X+0.69370\ Y+0.68057\ Z-0.52248=0$
Se_1 0.002; C_1 −0.028; N_1 0.017; Se_2 0

Table 6. Distances (Å) from the cesium ion to neighbouring nitrogen atoms. Standard deviations are given in parentheses.

$Cs\cdots N_{1A}$	3.23(2)	$Cs\cdots N_{2A}$	3.286(10)
$Cs\cdots N_{1B}$	3.23(2)	$Cs\cdots N_{2B}$	3.286(10)
$Cs\cdots N_{1C}$	3.20(2)		
$Cs\cdots N_{1D}$	3.20(2)		

are the same as found in the corresponding potassium and rubidium salts,[2,3] and in potassium selenocyanate.[10]

In potassium and rubidium triselenocyanate, each selenium atom has two selenium-selenium contacts to atoms in adjacent triselenocyanate ions. The Se···Se distances are in the range 3.467 to 3.602 Å. One of the selenium atoms involved in these contacts approaches the fourth coordination site of a square-planar four-coordination at the central selenium atom. There is no such approach in the present structure. The shortest non-bonding distances are from the central selenium atom, Se_2, to Se_2'' $(1-x,\bar{y},\bar{z})$ and to Se_2''' $(1-x,\bar{y},1-z)$; both are 3.674(3) Å. The angles $C_2-Se_2\cdots Se_2''$ and $C_2-Se_2\cdots Se_2'''$ are both 130.43(4)°.

The cesium ion lies on the twofold axis at $(0,y,1/4)$. The closest contacts of the ion are listed in Table 6. In the table a subscript A denotes an atom located at $(\frac{1}{2}-x,\frac{1}{2}-y,\bar{z})$, B at $(x-\frac{1}{2},\frac{1}{2}-y,z+\frac{1}{2})$, C at $(x,y,z+1)$, and D at $(\bar{x},y,\bar{z}-\frac{1}{2})$, where x, y, z are the atomic coordinates of Table 1. The cesium ion is surrounded by six nitrogen atoms at distances from 3.20 to 3.29 Å. The sum of the ionic radii of cesium and nitrogen is 3.40 Å.[11] The shape of the resulting polyhedron is a rather irregular trigonal prism.

Each of the nitrogen atoms has close contacts to two cesium ions. Those involving the nitrogen atom of the middle selenocyanate group occur in the a plane at $x=\frac{1}{2}$ and are to the cesium atoms at $(\frac{1}{2}-x,\frac{1}{2}-y,\bar{z})$ and $(\frac{1}{2}-x,\frac{1}{2}-y,1-z)$. The N···Cs distances are 3.29 Å and the Cs···N···Cs angle is 116.7°. The nitrogen atom of the terminal selenocyanate group has close contacts to Cs_A and Cs_D. The N···Cs distances are 3.23 and 3.20 Å, the Cs···N···Cs angle is 95.3, and the C—N···Cs angles are 130.0 and

131.3°. The carbon atom, the nitrogen atom, and the two cesium ions are almost coplanar.

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