la molécule sont particulièrement faibles: C(4)–C(5) 2,30 Å; C(5)–O(2) 2,64 Å; C(4)–N 2,39 Å; C(5)–N 2,43 Å.

L'enchaînement de la structure

Les molécules qui, toutes, se déduisent les unes des autres par de simples translations de réseau, forment des chaînes parallèles à l'axe cristallographique *a* (Fig 3).

Dans une chaîne, les molécules sont reliées par des liaisons hydrogène O(1)H···O(2). L'arrangement de ces chaînes moléculaires est représenté sur la Fig. 4 qui est une section par un plan perpendiculaire à l'axe *a*.

La cohésion entre les chaînes est assurée par des liaisons de van der Waals. Les distances interatomiques intermoléculaires les plus courtes sont: pour les molécules I et II (ou III et IV: numérotation de la Fig. 4):

$C(5_{II})O(1_I)$	3,60 Å
$C(5_{II})C(1_I)$	3,76
$O(2_{II})C(1_I)$	3,41
$O(2_{II})C(4_I)$	3,79

pour les molécules I et IV:

$C(5_{IV})C(4_I)$	3,70 Å

Cet enchaînement est tout à fait conforme à la morphologie; le bas point de fusion (73 °C) s'explique compte tenu de la faible cohésion de ce cristal; liaisons hydrogènes (O(1)···O(2) = 2,94 Å) et liaisons de van der Waals relativement longues.

Chaque molécule a dix molécules voisines; deux à la distance $c = 5{,}8$ Å, deux à la distance $|\mathbf{a}+\mathbf{c}| = 6{,}6$ Å, deux à la distance $a = 7$ Å et quatre à la distance $|(\mathbf{b}+\mathbf{a})/2| = 7{,}85$ Å.

L'arrangement des molécules dans le plan (a,c) est très proche d'un arrangement hexagonal compact, mais l'empilement de ces plans, lui, n'est pas compact (et de ce fait, l'arrangement des chaînes ne l'est pas non plus).

Nous remercions Mesdemoiselles Candy et Puthon qui, au cours de D.E.S., ont obtenu les données expérimentales de ce travail, et Monsieur Bassi et ses collaborateurs qui ont effectué les calculs numériques.

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The Crystal Structure of the Hydrated Caesium Fluoride–Thiourea Complex

By J. C. A. Boeyens

Chemical Physics Group of the National Physical and National Chemical Research Laboratories,
Council for Scientific and Industrial Research, Pretoria, South Africa

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The crystal structure of the complex, $CsF.4(SCN_2H_4).2H_2O$ has been determined by three-dimensional X-ray diffraction methods. Caesium ions were found to lie in a column, segregated from the fluoride ions and enclosed by the thiourea molecules in such a manner that each caesium ion lies at the centre of a slightly distorted cube defined by eight sulphur atoms. Each fluoride ion was found to be hydrogen-bonded in an octahedral fashion to two water molecules and the amine groups of two thiourea molecules.

Introduction

Thiourea, $S=C(NH_2)_2$, forms a series of structurally related ionic complexes with salts of potassium, rubidium, caesium, ammonium, thallium(I) and lead(II), which can be classified into a number of isomorphous groups (Boeyens & Herbstein, 1966). Because of a lack of suitable single crystals the structure type of the complexes formed by the chlorides of these cations has not yet been established. These complexes crystallize in the space group *Bbam* (D_{2h}^{18}) and have cell dimensions of $a \simeq 32$, $b \simeq 13$, $c \simeq 8{\cdot}5$ Å. The caesium fluoride complex, with space group *Ibam* and cell dimensions of $a = 17{\cdot}09$, $b = 12{\cdot}56$, $c = 8{\cdot}51$ Å, is, however, easily obtainable in the form of good single crystals and appears to be structurally closely related to the chloride complexes. The structure of the CsF complex was therefore determined in the hope that the structure type of the chloride complexes could be derived from it. Although this proved not to be the case, the present structure showed some interesting features, not encountered before in this series of complexes.

Experimental

Crystals of the complex were obtained from an aqueous solution of the components in 1:4 stoichiometric proportion. The crystals are orthorhombic and the unit-cell data, as reported before (Boeyens & Herbstein, 1967) are as follows: $a = 17{\cdot}09$, $b = 12{\cdot}56$, $c = 8{\cdot}51$ Å. The density, calculated for four formula units per unit cell, is 1·82 g.cm^{-3} and the measured density is 1·84 g.cm^{-3}. The conditions for possible reflexions are: hkl for $h+k+l=2n$, $0kl$ for $k=2n$, $h0l$ for $h=2n$. On this basis the centrosymmetric space group *Ibam* was selected and the choice was vindicated by the successful structure analysis.

A needle-shaped crystal of average diameter 0·01 cm and Cu $K\alpha$ (Ni filter) radiation were used at room temperature to collect non-integrated intensity data for 859 reflexions (including 125 unobserved). Standard multiple-film equi-inclination Weissenberg techniques were used and intensities were visually estimated. A value of $\frac{1}{3}I_{\text{min}}$ was assigned to unobserved reflexions (Hamilton, 1955) and the usual corrections were applied with the use of appropriate computer programs. The unobserved reflexions appear in Table 2 with $F_{\text{obs}} < 10$.

Determination and refinement of the structure

From the corrected intensities a three-dimensional Patterson synthesis was calculated with the computer program MIFR 1 of Shoemaker and Sly for the IBM 704 machine. The Cs–Cs vectors were easily identified and the other peaks defined the S, F, O, N and C positions relative to Cs, which could be placed in any of the fourfold positions: a $(0,0,\frac{1}{4};\ 0,0,\frac{3}{4})$ or c $(0,0,0;\ 0,0,\frac{1}{2})$. Since all the other atoms except N were seen to lie in a mirror plane normal to [001] [positions (j)] at a level $c/4$ from the Cs, the Cs had to be assigned to positions (a). The notation used here is that of *International Tables for X-ray Crystallography* (1952) for space group no. 72.

The atomic coordinates derived from the Patterson synthesis were refined by least-squares methods, using the full-matrix computer program ORXLS of Busing and Levy for the IBM 704 machine and the atomic scattering factors of Hanson, Herman, Lea & Skillman (1964). The quantity minimized is $\Sigma w(F_o - F_c)^2$. Because of the high relative mass of Cs and the fact that the intensities of all layer lines with l odd were uniformly very low, no attempt was made to weight the structure factors differentially and $w = 1$ was used for all (observed and unobserved) reflexions. After four cycles of refinement, using individual isotropic temperature factors, the parameter shifts were less than 0·1 of the estimated errors and convergence was considered as complete with $R = 0{\cdot}085$. A completely featureless three-dimensional difference synthesis confirmed the structure. The final atomic parameters are listed in Table 1 together with the observed and calculated structure factors, which are on an absolute scale, $F(000) = 896$, in Table 2.

Table 1. *Fractional coordinates and temperature factors* (Å^2) *of the atoms in the asymmetric unit, with estimated standard deviations below each value*

	x	y	z	B
Cs	0	0	$\frac{1}{4}$	3·10
				0·04
F	$\frac{1}{2}$	0	0	6·29
				0·40
S(1)	0·1402	0·1432	0	3·15
	0·0002	0·0003		0·08
S(2)	0·1047	0·1949	$\frac{1}{2}$	2·94
	0·0003	0·0003		0·08
C(1)	0·0949	0·2644	0	2·89
	0·0009	0·0011		0·28
C(2)	0·1957	0·1332	$\frac{1}{2}$	3·03
	0·0009	0·0011		0·28
N(1)	0·0770	0·3151	0·1378	4·08
	0·0005	0·0007	0·0015	0·20
N(2)	0·2300	0·1068	0·6348	4·13
	0·0005	0·0007	0·0014	0·21
O	0·3494	0·0458	0	5·63
	0·0008	0·0010		0·32

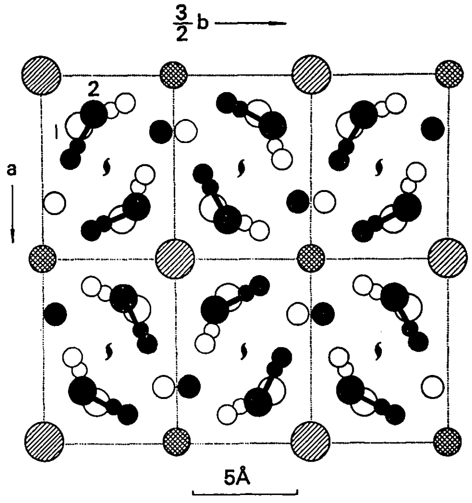

Fig. 1. Projection of the structure along [001]. Open circles indicate atoms belonging to molecules lying in the mirror plane in the paper and full circles refer to the mirror $c/2$ above the plane of the paper. The large shaded circles represent caesium ions at $c = \frac{1}{4}$, $\frac{3}{4}$ and the smaller, doubly shaded circles indicate fluoride ions at $c = 0$, $\frac{1}{2}$. Some essential symmetry elements are shown for clarity.

Description of the structure

The (001) projection (Fig. 1) provides the most illuminating view of the structure. The two independent sulphur atoms are, within experimental error, equidistant from the caesium. This separation of 2·69 Å is interpreted as a purely ionic contact. The thiourea molecules surrounding any stack of caesium ions, are, within experimental error, related by a local fourfold axis of symmetry which coincides with the stack axis. Furthermore the separation of the sulphur atoms of the thiourea molecules, which overlap in the (001) projection, is virtually the same as the shortest sulphur–sulphur distance in the (001) plane. The sulphur polyhedron can thus be described as a cube, twisted about the vertical fourfold axis by 16° and having the caesium ion as its centre. Although the arrangement of caesium ions can formally be considered as a column enclosed in a channel defined by the sulphur atoms, it differs from the true thiourea channel adducts (Hermann & Lenné, 1952) in that the thiourea framework is not held together by hydrogen bonds.

The only hydrogen bonds occur between the fluoride ion and the water molecules which are enclosed together in another channel defined by the amine groups of the thiourea molecules. The environment of a fluoride ion is shown in [010] projection in Fig. 2. The interatomic distances clearly show that the fluoride is definitely hydrogen-bonded to two water molecules and most probably to the $-NH_2$ groups of two thiourea molecules as well. Additional hydrogen bonding between a water molecule and the $-NH_2$ groups of the thiourea molecules not in contact with the fluoride is also not excluded, as the O–N distance of 3·03 Å is well within the range given by Pimentel & McClellan (1960). It was, however, not possible to determine the hydrogen positions in this structure experimentally.

The differences are not significant and are probably due to systematic errors or diffraction effects of the heavy Cs atom.

Table 2. *Observed and calculated structure factors on absolute scale*

H	F_o	F_c
L = 0, K = 0		
0	–	896
2	169	172
4	32	15
6	74	77
8	226	226
10	146	143
12	116	117
14	109	106
16	35	41
18	41	37
20	58	57
L = 0, K = 1		
1	214	205
3	100	87
5	201	185
7	122	122
9	186	183
11	59	58
13	66	73
15	55	61
17	49	54
19	30	38
21	39	46
L = 0, K = 2		
0	80	77
2	126	128
4	340	323
6	308	297
8	164	153
10	61	56
12	88	89
14	106	101
16	66	74
18	42	48
20	23	25
L = 0, K = 3		
1	76	76
3	306	331
5	135	139
7	32	27
9	42	46
11	134	139
13	91	95
15	69	71
17	48	58
19	13	25
L = 0, K = 4		
0	76	77
2	265	302
4	148	148
6	139	134
8	117	104
10	161	159
12	123	118
14	39	35
16	46	47
18	61	65
20	35	37
L = 0, K = 5		
1	105	113
3	142	145
5	69	61
7	156	161
9	110	122
11	117	118
13	20	13
15	25	30
17	49	52
19	59	64
L = 0, K = 6		
0	224	226
2	198	195
4	64	58
6	127	130
8	115	115
10	100	96
12	82	74
14	72	77
16	54	56
18	24	28
20	30	36
L = 0, K = 7		
1	147	145
3	51	49
5	119	116
7	119	127
9	45	50
11	32	33
13	87	84
15	77	84
17	7	16.
19	5	11
L = 0, K = 8		
0	107	101
2	66	59
4	156	153
6	147	147
8	103	99
10	46	42
12	42	45
14	70	76
16	54	49
18	9	15
L = 0, K = 9		
1	98	97
3	73	73
5	96	96
7	53	48
9	73	70
11	42	48
13	58	60
15	31	34
17	38	38
L = 0, K = 10		
0	104	100
2	109	96
4	112	103
6	14	12
8	65	65
10	103	99
12	59	60
14	7	11
16	27	26
L = 0, K = 11		
1	64	58
3	79	75
5	55	50
7	43	44
9	70	74
11	60	60
13	27	25
15	16	−0
L = 0, K = 12		
0	29	34
2	75	70
4	84	74
6	61	53
8	39	40
10	45	37
12	47	42
14	31	35
L = 0, K = 13		
1	51	42
3	41	45
5	59	57
7	66	59
9	12	8
11	6	15
L = 0, K = 14		
0	54	45
2	46	40
4	30	25
6	70	61
8	48	43
10	21	20
L = 0, K = 15		
1	62	56
3	6	15
5	5	12
7	37	36
L = 0, K = 16		
0	37	43
2	33	34
L = 1, K = 1		
2	28	−25
4	59	−45
6	22	30
8	73	−67
10	32	29
12	60	66
14	8	2
16	56	−55
18	8	−9
20	23	23
L = 1, K = 2		
1	54	58
3	22	−19
5	156	151
7	66	−60
9	114	−108
11	48	42
13	54	54
15	25	−25
17	25	−26
19	13	15
L = 1, K = 3		
2	16	14
4	30	−30
6	69	69
8	24	−24
10	23	−16
12	22	−17
14	25	18
16	8	2
18	8	6
20	6	−5
L = 1, K = 4		
1	57	−67
3	121	−135
5	5	−2
7	56	54
9	61	61
11	22	−22
13	50	−43
15	8	8
17	20	24
19	7	−1
21	15	−16
L = 1, K = 5		
2	68	72
4	25	−26
6	68	−66
8	83	77
10	22	17
12	62	−61
14	8	−3
16	32	31
18	7	2
L = 1, K = 6		
1	22	26
3	103	128
5	31	−31
7	71	−65
9	7	−0
11	14	17
13	8	9
15	8	3
17	8	−8
19	6	−10
L = 1, K = 7		
2	42	42
4	22	15
6	64	−63
8	7	−1
10	8	6
12	38	35
14	8	3
16	8	−16
18	24	−19
L = 1, K = 8		
1	64	−68
3	35	−33
5	37	36
7	32	32
9	41	−33
11	8	2
13	8	7
15	14	−12
17	6	4
L = 1, K = 9		
2	60	−68
4	8	−11
6	69	67
8	8	10
10	39	−35
12	8	−6
14	14	−6
16	11	8
18	13	14
L = 1, K = 10		
1	14	−9
3	37	−31
5	20	15
7	14	10
9	8	−12
11	8	7
13	13	5
15	11	−4
17	4	−1
L = 1, K = 11		
2	47	46
4	8	2
6	29	−23
8	15	−19
10	25	17
12	7	7
14	6	5
L = 1, K = 12		
1	43	42
3	35	31
5	25	−18
7	29	−26
9	24	18
11	7	0
13	6	−6
L = 1, K = 13		
2	8	2
4	8	−9
6	14	−10
8	18	15
10	19	12
12	18	−17
L = 1, K = 14		
1	13	−13
3	18	−14
5	7	1
7	15	13
9	9	8
L = 1, K = 15		
2	23	−18
4	6	7
6	19	14
L = 2, K = 0		
2	192	−178
4	362	−363
6	124	−111
8	44	−42
10	90	−81
12	94	−101
14	72	−72
16	68	−74
18	44	−55
20	6	−3
L = 2, K = 1		
1	139	−166
3	244	−240
5	237	−212
7	163	−151
9	122	−107
11	113	−111
13	101	−102
15	56	−56
17	55	−62
19	39	−43
21	15	−21
L = 2, K = 2		
0	220	−242
2	172	−178
4	92	−76
6	75	−60
8	157	−144
10	152	−153
12	76	−77
14	32	−37
16	36	−42
18	47	−51
20	44	−48
L = 2, K = 3		
1	295	−332
3	54	−50
5	91	−99
7	208	−198
9	149	−149
11	94	−86
13	73	−76
15	63	−71
17	29	−35
19	48	−49
21	32	−45
L = 2, K = 4		
0	176	−171
2	104	−99
4	103	−103
6	174	−174
8	115	−113
10	52	−54
12	53	−48
14	89	−95
16	60	−65
18	8	−16
20	25	−33
L = 2, K = 5		
1	111	−120
3	156	−154
5	197	−199
7	147	−142
9	63	−62
11	66	−65
13	90	−90
15	84	−87
17	28	−34
19	15	−18
L = 2, K = 6		
0	58	−60
2	124	−127
4	149	−146
6	88	−84
8	64	−56
10	84	−83
12	73	−83
14	43	−50
16	41	−43
18	33	−38
L = 2, K = 7		
1	113	−104
3	171	−174
5	91	−88
7	58	−58
9	121	−112
11	107	−111
13	36	−40
15	8	−16
17	62	−59
19	35	−46
L = 2, K = 8		
0	102	−95
2	106	−105
4	87	−75
6	51	−51
8	83	−87
10	89	−91
12	59	−60
14	8	−14
16	17	−28
18	45	−53
L = 2, K = 9		
1	101	−102
3	99	−93
5	83	−74
7	77	−75
9	76	−74
11	61	−56
13	54	−52
15	30	−39
17	21	−29
L = 2, K = 10		
0	103	−92
2	56	−51
4	59	−60
6	108	−100
8	61	−59
10	9	−10
12	41	−39
14	74	−70
16	26	−34
L = 2, K = 11		
1	71	−62
3	56	−52
5	93	−88
7	83	−77
9	38	−36
11	13	−19
13	40	−43
15	53	−53
L = 2, K = 12		
0	84	−81
2	50	−49
4	33	−33
6	50	−48
8	55	−49
10	44	−44
12	21	−29
L = 2, K = 13		
1	65	−62
3	65	−53
5	24	−23
7	18	−22
9	66	−57
11	60	−55
L = 2, K = 14		
0	18	−21
2	49	−45
4	52	−47
6	25	−24
8	23	−24
L = 2, K = 15		
1	10	−11
3	57	−51
L = 3, K = 1		
2	47	45
4	81	75
6	4	7
8	64	−63
10	46	−43
12	61	64
14	7	−2
16	22	−24
18	7	−6
20	20	21
L = 3, K = 2		
1	90	−88
3	6	3
5	7	17
7	5	1
9	77	−76
11	59	64
13	46	49
15	38	−40
17	25	−25
19	6	5
L = 3, K = 3		
2	39	−39
4	10	−13
6	16	12
8	32	31
10	37	−34
12	20	17
14	7	−8
16	13	9
18	6	−5
20	8	1
L = 3, K = 4		
1	41	−46
3	4	−2
5	14	16
7	48	47
9	6	6
11	45	−44
13	36	−37
15	18	20
17	36	36
19	5	−2
L = 3, K = 5		
2	34	35
4	52	−52
6	47	−51
8	62	69
10	40	37
12	56	−53
14	7	−4
16	12	18
18	6	1
L = 3, K = 6		
1	52	52
3	31	33
5	20	−19
7	70	−68
9	33	31
11	27	24
13	13	6
15	7	−1
17	24	−18
19	4	−5
L = 3, K = 7		
2	75	83
4	32	32
6	22	−19
8	49	−48
10	7	5
12	7	4
14	28	24
16	15	−13
18	4	−6
L = 3, K = 8		
1	32	−30
3	58	−60
5	50	48
7	17	15
9	25	−18
11	7	1
13	7	5
15	6	−9
17	5	−1
L = 3, K = 9		
2	79	−80
4	36	−35
6	60	58
8	22	17
10	13	−12
12	7	−3
14	6	−8
16	5	−2
L = 3, K = 10		
1	12	−9
3	7	2
5	13	18
7	7	10
9	31	−26
11	7	−2
13	6	5
15	5	1
L = 3, K = 11		
2	43	40
4	13	14
6	35	−30
8	7	−8
10	7	2
12	14	14
14	7	−1
L = 3, K = 12		
1	18	14
3	28	27
5	39	−37
7	17	−12
9	24	22
11	9	9
13	4	−5
L = 3, K = 13		
2	7	6
4	11	2
6	6	−13
8	13	15
10	4	1
L = 3, K = 14		
1	10	−10
3	6	−8
5	9	4
7	4	10
L = 3, K = 15		
2	23	−22
L = 4, K = 0		
2	174	162
4	52	−24
6	199	194
8	183	174
10	124	116
12	55	51
14	47	50
16	39	39
18	27	31
20	52	64
L = 4, K = 1		
1	176	167
3	119	102
5	84	61
7	131	114
9	102	86
11	97	89
13	49	48
15	76	72
17	26	29
19	28	32
L = 4, K = 2		
0	87	107
2	146	153
4	166	172
6	158	158
8	72	69
10	55	52
12	92	88
14	94	92
16	61	62
18	23	28
20	8	15
L = 4, K = 3		
1	26	−10
3	183	194
5	169	183
7	75	66
9	81	74
11	73	68
13	63	61
15	36	37
17	55	57
19	18	28
L = 4, K = 4		
0	121	140
2	116	128
4	156	166
6	47	49
8	106	98
10	106	109
12	84	93
14	28	32
16	31	31
18	51	58
L = 4, K = 5		
1	149	157
3	91	88
5	52	44
7	47	37
9	123	120
11	74	78
13	57	58
15	16	16
17	50	48
19	24	36
L = 4, K = 6		
0	141	153
2	72	74
4	86	89
6	109	110
8	126	124
10	65	63
12	36	40
14	50	49
16	33	39
18	28	33
L = 4, K = 7		
1	97	96
3	48	41
5	101	100
7	108	109
9	47	43
11	28	22
13	59	61
15	61	65
17	6	14
L = 4, K = 8		
0	94	92
2	95	94
4	75	78
6	99	95
8	45	44
10	43	39
12	49	52
14	72	72
16	41	43
L = 4, K = 9		
1	59	54
3	73	70
5	73	69
7	73	72
9	43	40
11	48	51
13	14	25
15	32	35
L = 4, K = 10		
0	36	35
2	90	89
4	67	62
6	40	39
8	55	50
10	79	80
12	35	39
14	12	1
L = 4, K = 11		
1	70	65
3	75	67
5	16	19
7	22	23
9	44	48
11	62	61
13	25	26
L = 4, K = 12		
0	27	27
2	55	49
4	66	62
6	45	42
8	35	35
10	27	28
12	29	32
L = 4, K = 13		
1	28	24
3	27	31
5	64	60
7	53	50
9	16	17
L = 4, K = 14		
0	61	59
2	27	26
4	21	26
6	31	33
L = 5, K = 1		
2	17	15
4	39	31
6	11	6
8	53	−46
10	20	−16
12	51	50
14	9	−1
16	20	−25
18	6	−6
L = 5, K = 2		
1	28	−32
3	5	4
5	21	31
7	7	−10
9	59	−59
11	44	41
13	38	38
15	26	−27
17	18	−19
L = 5, K = 3		
2	26	−23
4	6	−8
6	27	20
8	8	11
10	25	−22
12	9	7
14	9	−1
16	8	6
18	6	−1
L = 5, K = 4		
1	26	−31
3	19	−25
5	14	2
7	39	37
9	20	18
11	34	−29
13	34	−30
15	15	13
17	20	25
L = 5, K = 5		
2	20	29
4	28	−29
6	35	−36
8	43	48
10	26	23
12	34	−41
14	9	−3
16	7	17
L = 5, K = 6		
1	37	37
3	40	42
5	24	−18
7	49	−49
9	21	18
11	15	16
13	9	5
15	7	1
17	9	−12
L = 5, K = 7		
2	45	48
4	25	20
6	21	−21
8	37	−28
10	9	5
12	9	11
14	13	14
16	6	−12
L = 5, K = 8		
1	29	−28
3	39	−39
5	34	32
7	15	15
9	15	−16
11	9	0
13	8	4
15	6	−7
L = 5, K = 9		
2	58	−58
4	27	−20
6	47	47
8	9	11
10	8	−14
12	7	−3
14	6	−7
L = 5, K = 10		
1	9	−7
3	9	−5
5	15	12
7	15	8
9	20	−17
11	7	0
13	5	4
L = 5, K = 11		
2	34	31
4	9	9
6	20	−22
8	8	−8
10	6	4
12	5	10
L = 5, K = 12		
1	20	16
3	19	22
5	26	−24
7	12	−12
9	17	16
L = 5, K = 13		
2	7	4
4	6	−1
6	10	−10
8	7	12
L = 5, K = 14		
1	8	−8
L = 6, K = 0		
2	112	−95
4	192	−173
6	110	−95
8	46	−33
10	55	−48
12	65	−56
14	45	−41
16	44	−48
18	22	−36
L = 6, K = 1		
1	74	−83
3	136	−127
5	110	−100
7	78	−76
9	61	−54
11	80	−73
13	53	−57
15	34	−38
17	26	−37
L = 6, K = 2		
0	121	−139
2	104	−105
4	48	−40
6	54	−39
8	89	−81
10	91	−91
12	54	−53
14	26	−28
16	21	−27
18	18	−31
L = 6, K = 3		
1	131	−147
3	36	−30
5	60	−62
7	104	−114
9	90	−93
11	46	−44
13	37	−40
15	33	−39
17	17	−24
L = 6, K = 4		
0	115	−111
2	57	−53
4	70	−67
6	100	−95
8	77	−74
10	32	−31
12	37	−32
14	52	−62
16	30	−40
L = 6, K = 5		
1	66	−74
3	80	−82
5	105	−108
7	68	−66
9	37	−38
11	37	−36
13	59	−64
15	45	−54
L = 6, K = 6		
0	37	−34
2	73	−65
4	102	−97
6	61	−57
8	45	−43
10	53	−51
12	44	−49
14	26	−30
16	20	−27
L = 6, K = 7		
1	60	−58
3	94	−96
5	51	−52
7	37	−36
9	63	−68
11	55	−67
13	15	−24
15	6	−9
L = 6, K = 8		
0	65	−63
2	80	−75
4	49	−42
6	26	−27
8	45	−48
10	56	−60
12	37	−41
14	6	−11
L = 6, K = 9		
1	58	−57
3	54	−55
5	46	−44
7	52	−53
9	34	−42
11	33	−36
13	24	−29
L = 6, K = 10		
0	54	−47
2	37	−35
4	41	−38
6	68	−68
8	32	−38
10	8	−8
12	16	−23
L = 6, K = 11		
1	46	−42
3	29	−32
5	49	−51
7	44	−46
9	17	−19
L = 6, K = 12		
0	51	−50
2	29	−31
4	24	−23
6	24	−31
8	20	−32
L = 6, K = 13		
1	31	−37
3	27	−31

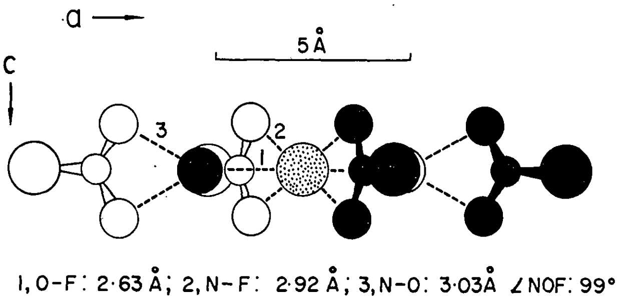

Fig. 2. (010) projection of the surroundings of a fluoride ion to indicate close approaches and possible hydrogen bonds. The shaded fluoride ion lies in the plane of the paper whereas open and full circles indicate atoms respectively above and below this plane. The numbers in the diagram refer to possible hydrogen bonds.

Except for the contacts shown in Fig. 2, all other intermolecular contacts are of the normal van der Waals type. The S–S distances in the (001) mirror plane are 4·29 ± 0·02 Å and 4·24 ± 0·02 Å, whereas the two different S–S–S angles for nearest neighbours are 89·3 ± 1 and 90·3 ± 1°. The shortest out-of-plane S–S distance is 4·30 ± 0·02 Å. The angle of twist about [001] of the one with respect to the other sulphur square is 16°.

Bond lengths and interatomic distances

Because of the presence of the heavy caesium atom all interatomic distances are given with caution. The two Cs–S distances of (1) 3·68 ± 0·01 Å and (2) 3·70 ± 0·01 Å should thus be considered as identical. The interatomic distances (Å) for the two crystallographically distinct thiourea molecules are listed below, together with the values given by Kunchur & Truter (1958) for thiourea:

	S–C	C–N	S–N
(1)	1·71 ± 0·02	1·36 ± 0·02	2·68 ± 0·02
(2)	1·73 ± 0·02	1·33 ± 0·02	2·67 ± 0·02
KT	1·71 ± 0·01	1·33 ± 0·01	

	N–N	NCN
(1)	2·35 ± 0·02	118 ± 2°
(2)	2·30 ± 0·02	119 ± 2°
KT		115·6 ± 1·1°

Discussion

This structure is closely related to the previously reported structures of this type of complex (Boeyens & Herbstein, 1966, 1967). It differs from them significantly in being orthorhombic as opposed to tetragonal and in being almost completely ordered at room temperature. These two effects both arise from the existence of the system of hydrogen bonds around the anion. The tendency of the anion to be positionally disordered in the channel is still apparent in the relatively high temperature factors calculated for fluorine and oxygen, but since the anion is hydrogen-bonded to the walls of the channel the degree of ordering is much higher than that of the nitrate ion in the $TlNO_3$.4(thiourea) complex. The hydration of the anion is necessitated by its small size, which would entail very loose contacts in the usual type of tetragonal channel, described before and also by its tendency to form strong hydrogen bonds. The water therefore serves to provide the necessary close contact between the fluoride and the channel walls without having contraction of the channel whereby the –NH_2 groups would be brought uncomfortably close together. Effectively the included anion is thus the doubly hydrated fluoride ion which is considerably elongated, causing a parallel elongation of the channel which leads to orthorhombic rather than tetragonal symmetry. The structural role of the water is thus entirely different from that of the zeolitic water in the hydrated 6:1 thiourea complex of $Pb(ClO_4)_2$ (Boeyens & Herbstein, 1967).

Conclusion

It was expected that the arrangement of thiourea molecules around the caesium ion as found in this CsF-complex, together with the symmetry operators of space group *Bbam* would lead directly to the structure of the CsCl.4 (thiourea) complex, the cell dimensions of which are simply related to those of the present complex (Boeyens & Herbstein, 1966). Because of the prominent structural role of water found here, however, the two types of structure now seem to be completely different.

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