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The Crystal Structure of Potassium Trithiocarbonate Monohydrate, $K_2CS_3.H_2O$

By Etienne Philippot* and Oliver Lindqvist

Department of Inorganic Chemistry, Chalmers University of Technology and the University of Göteborg, Kemigården 3, *P.O. Box* S-402 20, *Göteborg* 5, *Sweden*

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The crystal structure of $K_2CS_3.H_2O$ has been determined. It belongs to the space group $P2_1/n$ and there are four formula units in the cell, which has the dimensions $a=6{\cdot}759$, $b=17{\cdot}066$, $c=6{\cdot}418$ Å and $\beta=95{\cdot}42°$. The structure was solved by means of the symbolic addition method and 1166 independent reflexions were refined to an R value of 0·067. The trithiocarbonate anion has, within the significance interval, a planar and regular configuration, the three C–S bond distances being 1·708, 1·709 and 1·720 Å with a mean value of 1·712 Å.

Introduction

The literature contains crystal structure determinations for only two substances containing CS_3^{2-} groups: trithiocarbonic acid, (at -100°C) and the complex compound $[(C_6H_5)_4As]_2[Ni(CS_3)_2]$. The former was solved by Krebs & Gattow (1965) from $hk0$, $h0l$ and $0kl$ single-crystal data and was found to be built up of planar CS_3^{2-} groups which are held together by hydrogen bonds. The structure of $[(C_6H_5)_4As]_2[Ni(CS_3)_2]$ was determined from three-dimensional data by McKechnie, Miesel & Paul (1967) and contains complex ions $[Ni(CS_3)_2]^{2-}$ consisting of two planar CS_3^{2-} ions bound to a central nickel(II) ion. Owing to the bonds to the nickel(II) ion, the S–C–S angles deviate significantly from the ideal value of 120°.

A CS_3 grouping also occurs as a part of the molecule β-$C_3O_2S_3$, which was solved by Krebs & Koenig (1969) and was found to have an almost regular and planar arrangement of carbon and sulphur.

An infrared spectroscopic study of $K_2CS_3.H_2O$, performed by one of us (Philippot, 1967), showed some indication that the free CS_3^{2-} ions in this substance might be unsymmetrical. Since it was considered of interest to investigate a material containing free CS_3^{2-} ions and thus to ascertain the configuration of the ion, we decided to carry out a single-crystal structure analysis of $K_2CS_3.H_2O$.

Experimental

Crystals of $K_2CS_3.H_2O$ are formed rapidly when diethyl ether is added to a saturated aqueous solution of potassium trithiocarbonate. The monohydrate is very unstable towards atmospheric moisture, the stability range being $2 \le p_{H_2O} \le 5$ mmHg (Maurin & Silber, 1964).

The crystal data for $K_2CS_3.H_2O$ are given in Table 1. The unit-cell dimensions and the values of D_m and D_x have been obtained from a previous study (Philippot, Ribes & Maurin, 1969). The space group was determined from Weissenberg photographs showing systematic absences for $h0l$ when $h+l=2n+1$ and for $0k0$ when $k=2n+1$.

A crystal of size $0{\cdot}48 \times 0{\cdot}16 \times 0{\cdot}16$ mm was selected for the data collection and was sealed in a capillary tube, the manipulation being carried out under xylene to exclude air. The reflexions $0kl-6kl$ were registered with the multiple-film equi-inclination Weissenberg technique, using Cu $K\alpha$ radiation. The intensities were estimated visually with the aid of an intensity scale prepared from timed exposures of a chosen reflexion of the actual crystal. The number of independent reflexions was 1396 (91 % of the copper radiation sphere), of which 218 were too weak to be measured.

The intensity values from the six films recorded for each layer line were scaled together by means of the program *SCALE* (Hamilton, Rollett & Sparks, 1965) using artificial weights according to the formula

$$w=\frac{1}{1{\cdot}0+[(I-12{\cdot}0)/6{\cdot}0]^2}\,.$$

Correction for absorption and the calculation of Lorentz and polarization factors were performed with the program *DATAP*2. The absorption correction was not made until an approximate structure had been devised. The absolute scale and overall temperature factor ($B=2{\cdot}27$ Å^2, before absorption correction) were estimated by Wilson's (1942) method.

Determination of the structure

The structure was solved by means of the symbolic addition procedure (Hauptman & Karle, 1953; Karle & Karle, 1966) using the program system *GAASA* (Lindgren, Lindqvist & Nyborg, 1970).

Normalized structure factors $|E|$ were calculated for all observed and unobserved reflexions and the cor-

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* Present address: Laboratoire de Chimie Minérale, Faculté des Sciences, Place Eugène Bataillon, 34-Montpellier, France.

responding E statistics are in good agreement with the theoretical values for centrosymmetric structures:

	$\langle\lvert E\rvert\rangle$	$\langle\lvert E\rvert^2\rangle$	$\langle\lvert E^2-1\rvert\rangle$
Theoretical:	0·798	1·000	0·968
Observed:	0·820	1·008	0·939 .

The phases of ten large $|E|$ values were assigned symbols *a–j*, as shown in Table 2. 245 reflexions with $|E|>1{\cdot}4$ were used in the symbolic addition procedure, but only those having $|E|>1{\cdot}5$ were allowed in the $\sum_2$-listing for each reflexion. After three cycles of symbolic addition, seven symbols were solved and the signs of 234 $|E|$ values were expressed in terms of the symbols *h*, *i* and *j* (the signs of 35 structures invariants were explicitly determined). After choosing these three symbols to be positive, thereby specifying the origin, a three-dimensional Fourier synthesis was calculated on the basis of the 234 phased E values. In this, all the potassium and sulphur atoms were readily located. Their positions were then used to calculate a difference Fourier summation with all 1178 observed structure factors, thus giving the oxygen and carbon atom coordinates.

A later check showed that all 234 $|E|$ values had been assigned correct phases, and that the carbon and oxygen atoms had, in fact, been clearly resolved in the original E map. However, two spurious peaks of the same order of magnitude had also appeared (Fig. 1).

Refinement

The positional parameters, isotropic temperature factors and separate scale factors for the seven layer lines were initially refined. After three cycles, using the full-matrix least-squares program *LALS*, the R index ($=\sum||F_o|-|F_c||/\sum|F_o|$) became 0·126. After the absorption correction had been applied, another three cycles of refinement were performed, giving more reliable temperature and scale factors ($R=0{\cdot}115$).

In the final refinement, an overall scale factor was introduced, and all atoms were refined anisotropically. Atomic scattering factors as given by Cromer & Waber (1965) and weights according to the formula $w=(10{\cdot}0+|F_o|+0{\cdot}015|F_o|^2)^{-1}$ were used. The unobserved reflexions were excluded from the last cycles of refinement, as were ten strong reflexions which were considered to be affected by extinction and two other reflexions with very ill-defined spots on the Weissenberg films. After six cycles, the largest shift was not more than 4% of the corresponding standard deviation, and the final residual for 1166 observed reflexions was 0·067 [0·095 including all reflexions, unobserved intensities being given half the value of $I_{\text{obs}}(\text{min})$]. The observed and calculated structure factors are listed in

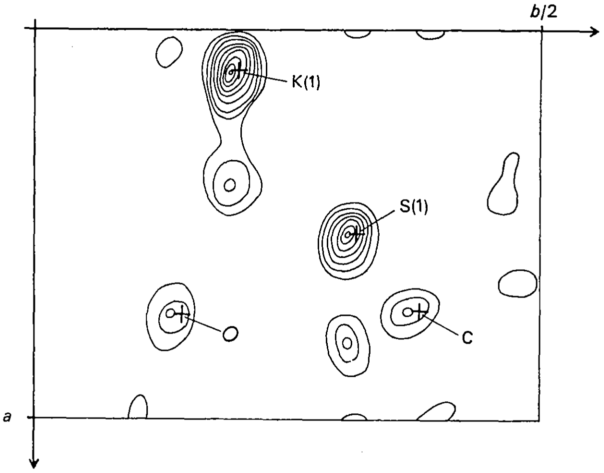

Fig. 1. An E-map section through $z/c=0{\cdot}08$ showing the positions of K(1), S(1), O, C and the two spurious peaks.

Table 1. *Crystal data for* $K_2CS_3.H_2O$

Unit-cell dimensions:	$a=\ 6{\cdot}759\pm0{\cdot}005$ Å
	$b=17{\cdot}066\pm0{\cdot}004$
	$c=\ 6{\cdot}418\pm0{\cdot}002$
	$\beta=95{\cdot}42\ \pm0{\cdot}05°$
	$U=737{\cdot}0$ Å^3
	$Z=\ 4$
Formula weight:	204·42
Density (20°C)	$D_m=1{\cdot}82$ g.cm^{-3}
	$D_x=1{\cdot}83$ g.cm^{-3}
Space group:	$P2_1/n$
General point position:	$\pm(x,y,z);\ \pm(\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)$
Crystal habit:	Orange needles
Linear absorption coefficient:	$\mu=178$ cm^{-1} (Cu $K\alpha$, $\lambda=1{\cdot}5418$ Å)

Table 2. *The initial basic set used in the symbolic addition procedure*

h	*k*	*l*	*E*	Symbol
1	11	6	3·316	*a*
4	13	1	2·990	*b*
4	5	−2	2·871	*c*
4	11	−1	2·867	*d*
4	5	4	2·806	*e*
2	11	3	2·804	*f*
2	16	−2	2·708	*g*
4	2	5	2·536	*h*
6	13	−1	2·503	*i*
1	2	−4	2·499	*j*

Table 3. *Observed and calculated structure factors*

The columns are k, $10|F_o|$ and $10F_c$. * Indicates unobserved reflexions. ** Indicates reflexions affected by extinction.

0 K 0		
4	303	-273
6	753	789
8	607	-604
10	345	-363
12**	834	-860
14	274	-271
16	160	166
18	210	-206
20	97	89
0 K 1		
1	353	-376
2	381	422
3	240	270
4**	835	1065
5	350	355
6	844	948
7	507	-522
8	639	639
9	133	121
10	129	118
11	72	68
12	53	86
13	61	56
14	139	-151
15	54	47
16	408	-414
17	181	-178
18	190	-161
19	234	212
20	143	-127
0 K 2		
0	310	287
1	567	-668
2**	1049	-1405
3	315	316
4	728	-830
5	65	43
6	473	500
7	416	-461
8	246	212
9	355	407
10	516	556
11	268	-258
12	227	238
13	135	-126
14	332	318
15	154	143
16	276	280
17*	47	-32
18	183	-159
19	43	39
20	99	-97
0 K 3		
1	33	23
2	679	-690
3	102	95
4	329	-374
5	128	107
6	466	-483
7	53	-78
8	371	-397
9	77	74
10	446	-488
11*	54	-23
12	229	227
13	70	-69
14	291	283
15*	50	-39
16	85	-74
17	105	-97
18	310	301
19*	31	27
20	131	140
0 K 4		
0	401	408
1	441	-456
2	417	435
3	326	318
4	258	246
5	85	69
6*	50	15
7	336	-329
8	195	-202
9	492	508
10	316	-329
11	98	-97
12	223	-197
13	72	-68
14	204	-177
15	188	150
16	167	-124
17	70	-58
0 K 5		
1	59	44
2	59	-48
3	102	-113
4	340	344
5	142	-143
6	361	362
7	105	90
8	244	238
9*	52	-13
10	90	-85
11*	50	-11
12	154	124
13*	44	13
14*	40	23
15	76	67
16	222	-285
17	96	112
0 K 6		
0	659	-593
1	137	-123
2*	51	11
3	146	118
4*	50	18
5*	45	-18
6	188	-145
7	226	-193
8	146	122
9	160	121
10*	42	39
11	96	-79
12	268	247
13	108	-100
14	99	89
0 K 7		
1	93	78
2	133	-117
3	47	-42
4	99	-85
5	67	-53
6	75	-67
7	170	149
8	108	-88
9*	30	-22
10	123	-109
11	34	-30
0 K 8		
0	164	-150
1	32	27
2	180	171
3*	23	-1
4	103	93
1 K 0		
2	488	-467
3	622	-591
4	261	283
5**	868	967
6	102	103
7	644	-680
8	320	285
9	160	-141
10	55	-65
11	528	533
12	52	56
13	331	-329
14	259	283
15*	48	17
16	134	-119
17	100	89
18	72	-71
1 K 1		
0	117	93
1	339	340
2	184	-70
3	590	611
4	201	-196
5	755	-783
6	243	-242
7	372	-366
8	214	208
9	548	548
10*	43	-12
11	163	-161
12	246	-226
13	116	-103
14	376	328
15	62	-16
16	60	50
17	135	132
18*	40	-4
19	61	62
20	125	121
21	115	-115
1 K 2		
1	328	325
2**	659	-835
3	219	-218
4	677	716
5	354	382
6	285	-264
7	148	-135
8	41	29
9	284	-267
10	164	-158
11	102	95
12	269	-274
13	145	-142
14	268	278
15*	46	-36
16	203	-188
17*	41	37
18	71	-64
19*	32	-36
20	141	158
1 K 3		
0	115	-132
1	256	276
2	171	158
3	504	507
4	49	-30
5	276	-256
6	62	-54
7	121	120
8	215	226
9	416	410
10*	47	-16
11	160	-170
12*	48	-22
13*	47	-35
14*	46	-13
15	159	-141
16	94	-86
17	56	35
1 K 4		
1	147	-147
2	421	-461
3	150	-156
4	410	426
5	221	-226
6	215	-232
7	353	349
8*	46	-3
9	66	48
10	122	116
11*	47	-11
12	103	-82
13	205	205
14	214	223
16	52	-50
17*	29	-4
18	47	-49
1 K 5		
0	157	-158
1*	45	21
2	147	146
3	117	-112
4*	45	25
5	277	-283
6	75	-65
7	53	-37
8	65	-48
9*	45	-42
10	96	-89
11	116	-89
12	113	95
13	122	123
14	105	-97
15	44	39
1 K 6		
1	169	157
2*	44	-25
3	195	168
4	158	148
5	244	-256
6*	42	-34
7	179	190
8*	39	-17
9	84	-79
10	104	90
11	302	-275
12	71	-61
13	64	58
14	52	-44
1 K 7		
0	171	-146
1	45	43
2*	35	8
3*	34	15
4*	33	25
5	147	128
6*	31	15
7	168	156
8	31	-30
9	37	-36
1 K -1		
0	453	459
1	69	45
2	78	-85
3	256	249
4	155	145
5	363	-360
6	33	32
7	371	-356
8	155	155
9	382	337
10	49	46
11	44	-3
12	434	-419
13	127	-120
14	223	228
15	138	129
16	114	-113
17	51	49
18	234	-231
19*	36	-3
20	88	82
1 K -2		
1	267	-244
2	430	440
3	368	-373
4	585	-560
5	777	733
6	73	64
7	605	-594
8	71	-53
9	138	123
10	236	-247
11	571	589
12	68	66
13	237	-252
14	138	-128
15*	47	-4
16*	45	8
17	48	43
18	98	99
1 K -3		
0	137	162
1	96	-100
2	294	-287
3*	37	23
4	68	-45
5	471	486
6*	40	-3
7	123	121
8	43	-34
9*	45	-12
10	114	105
11	55	45
12	158	-143
13	172	-167
14	205	214
15	51	49
16	94	86
17	138	-142
18	90	-81
19	93	-99
20	73	82
1 K -4		
1	112	116
2	659	633
3	236	269
4	447	-472
5	164	174
6	187	185
7	327	-349
8	66	59
9	115	-110
10	48	33
11*	48	-5
12	174	189
13	164	-174
14	182	-213
15	72	-60
16	88	73
17	44	44
18	73	48
1 K -5		
0	125	144
1	175	-214
2*	46	-22
3	362	-392
4*	46	15
5	93	98
6	72	67
8	61	-63
9	271	-300
10*	46	31
11	94	91
12*	43	-28
13	83	70
14	62	-55
15	163	167
16	37	28
1 K -6		
1	237	-254
2	252	282
3	74	69
4	233	-255
5	146	-144
6*	44	12
7	105	101
8*	42	-15
9	135	146
10*	38	21
11	35	42
12	52	49
13	140	146
14	118	-132
1 K -7		
5	221	236
6*	34	26
7	148	144
8*	30	-30
9	75	-79
10*	24	14
11	43	46
2 K 0		
1	388	-368
2**	912	-1237
3	63	55
4	189	-174
5	636	-664
6	344	342
7	555	-580
8	217	-214
9	253	246
10	669	706
11	295	-286
12	415	415
13*	64	33
14	106	94
15	173	149
16	231	230
17	176	154
18	93	-93
19	141	131
20	88	-90
21	63	-70
2 K 1		
1	437	380
2**	916	-1056
3	668	669
4	195	-199
5	225	-245
6	601	-627
7	77	-44
8	398	-417
9	57	56
10	407	-412
11	453	-471
12	116	121
13	188	-176
14	371	380
15	90	-55
16	62	-24
17	87	-96
18	238	217
19	81	70
20	140	152
2 K 2		
0	289	294
1	254	-237
2	555	555
3	711	776
4	552	589
5	206	189
6*	51	1
7	146	-134
8	611	-611
9**	735	799
10	244	-246
11	106	-101
12*	65	-44
13	166	-143
14	370	-418
15*	61	8
16	74	-71
17	170	-154
18	104	105
19	45	-49
20	45	38
2 K 3		
1	306	-320
2	129	120
3	75	-79
4	358	399
5	465	-514
6	431	457
7	322	322
8	362	391
9	241	239
10	105	-105
11*	65	-55
12*	65	45
13	293	250
14*	60	-23
15	185	171
16	292	-281
17	74	69
18	59	-61
19	42	-49
2 K 4		
0	815	-824
1	233	-241
2	55	-45
3*	59	35
4*	61	-3
5	215	-202
6	125	-117
7	462	-475
8	127	137
9	97	98
10	342	136
11	126	-122
12	406	399
13	105	-107
14*	53	-19
15	186	146
16*	42	-33
17	40	41
2 K 5		
1	198	194
2*	62	40
3	153	155
4	346	-347
5	124	-105
6	151	-147
7	214	194
8	78	-74
9	119	-105
10	155	-137
11	233	-199
12*	51	60
13	65	-52
14	57	57
15	82	-94
2 K 6		
0	141	-122
1*	58	-11
2	274	285
3*	57	30
4	86	72
5	187	172
6	144	-133
7	95	79
8	57	52
9	61	61
10	186	-170
11	106	101
2 K 7		
1	66	-59
2	226	194
3	84	-80
4	57	-51
5	39	-40
6	82	79
7	39	42
8	67	65
2 K -1		
1	734	-703
2	425	-347
3*	34	18
4**	1015	1320
5	69	60
6	592	626
7	299	-287
8	330	328
9	434	426
10	205	193
11	236	235
12*	63	5
13	118	125
14*	65	-7
15	117	118
16	360	-378
17	101	-100
18	223	-201
19	102	96
20*	37	-4
2 K -2		
0**	1280	1733
1	214	237
2	98	87
3	218	216
4	155	148
5	202	179
6	337	331
7	445	444
8	472	-455
9	85	73
10	142	-137
11	65	-61
12	552	-572
13*	66	6
14	217	-206
15	203	-189
16	84	76
17*	54	-20
18	163	-151
19	59	-57
20	73	77
2 K -3		
1	110	78
2	641	-620
3	254	261
4	123	-121
5	434	434
6	451	-467
7	512	-550
8	531	-533
9	139	-139
10*	64	-30
11	76	60
12	66	-56
13	213	-168
14	139	121
15	55	-50
16	180	173
17	69	-61
18	94	82
19	144	153
2 K -4		
0	154	162
1	198	199
2	515	-531
3	331	-358
4	417	-449
5	176	-176
6	118	113
7	140	155
8	245	261
9	327	-367
10	221	235
11	112	105
12*	63	-20
13	186	170
14	327	298
15*	52	-40
16	198	178
17	107	108
18	86	-93
2 K -5		
1	169	-161
2	125	130
3	108	-122
4	200	212
5	221	256
6	209	246
7	143	-147
8	90	100
9*	63	17
10	265	248
11	279	267
12*	57	-33
13*	52	-13
14	125	-121
2 K -6		
0	188	220
1	151	153
2	184	181
3	93	-79
4*	60	-17
5	119	126
6*	58	-5
7	206	204
8	110	112
9	196	-203
10	181	-173
11	80	76
12	192	-191
2 K -7		
4	168	-164
5*	46	50
6	77	-72
7*	42	-29
8	92	-97
9	88	-92
3 K 0		
1	249	301
2	620	-597
3	525	-492
4	418	369
5	278	244
6	178	-152
7	209	195
8	81	-74
9	178	-168
10	294	-274
11	76	83
12*	39	-26
13	68	-72
14	156	188
15*	38	21
16	200	-235
17*	33	-2
18	96	91
19	150	-155
20	118	129
3 K 1		
0	663	-644
1	301	-262
2	482	439
3	202	190
4	231	221
5	70	46
6	268	-266
7	54	-34
8	238	236
9	259	240
10	94	-92
11	105	-100
12	51	48
13	56	60
14	45	-40
15*	38	4
16	214	-217
17*	32	2
18	55	52
19	30	-12
3 K 2		
1	97	93
2	333	-348
3	312	-330
4	373	388
5	216	-233
6	226	-233
7	366	389
8*	37	23
9	86	-88
10	168	169
11*	40	-26
12*	40	-25
13	80	91
14	160	367
15*	35	36
16	79	-67
17	135	126
18*	24	-9
19	109	-125
3 K 3		
0	582	-628
1	64	-55
2	328	348
3	203	-206
4	193	200
5	65	-61
6	266	-292
7	75	63
8	44	-21
9	219	-227
10	138	-143
11	55	-58
12	162	155
13	154	140
14	44	-34
15	31	-41
16	72	-69
17	39	37
18	127	151
3 K 4		
1	173	176
2*	37	19
3	119	110
4	191	199
5	234	-253
6	71	-70
7	247	252
8*	39	-17
9	85	-84
10	162	154
11	187	-198
12	164	-169
13*	32	27
14	85	-86
15	78	-76
17	45	68
3 K 5		
0	328	-320
1	131	136
2	43	40
3	71	-71
4	83	72
5	143	134
6*	38	-31
7	263	247
8*	35	33
9	172	-173
10	41	39
11	51	62
12	157	146
13	72	66
14	43	-45
3 K 6		
1	125	-112
2	32	32
3	45	42
4	121	-117
5	143	-140
6	59	-53
7	104	102
8	87	-74
9	73	71
10	83	86
3 K 7		
0	97	93
1	70	64
2	21	23
3	116	-116
4*	20	13
5	36	-40
3 K -1		
0	134	-147
1	298	-279
2	91	-73
3	515	495
4	238	-195
5	99	-74
6	182	-177
7	387	-383
8	221	223
9	493	501
10*	37	20
11	180	-175
12	39	-41
13	201	-210
14	199	208
15	44	38
16*	36	14
17*	33	5
18	65	60
19*	24	17
20	36	49
3 K -2		
1	278	264
2	261	-255
3	364	-322
4	210	191
5	435	403
6	384	374
7	251	-247
8	185	177
9	211	-201
10	265	-258
11	90	93
12	204	215
13	125	-137
14	145	162
15	60	70
16	269	-253
17*	31	-1
18*	27	4
19	31	29
3 K -3		
0	715	692
1	149	-148
2	71	-60
3	197	202
4	108	-96
5	277	-276
6	158	155
7	439	-479
8*	38	14
9	347	386
10	61	-59
11*	40	11
12	268	-284
13	148	-145
14	63	52
15	179	183
16*	31	-3
17	60	70
18	104	-110
19	18	10
3 K -4		
1	185	-191
2*	36	-34
3	136	-143
4	304	-321
5	210	223
6	104	96
7	157	-164
8	78	-81
9	138	145
10	255	-279
11	192	223
12	142	144
13*	35	-3
14	49	47
15	25	26
16	36	-23
17	73	-78
3 K -5		
0	280	303
1	63	66
2	300	-319
3	163	179
4	180	-184
5	120	123
6	180	198
7*	38	8
8*	38	-8
9	160	158
10	90	100
11*	35	25
12	32	-29
13	162	-173
14	108	104
15*	21	-4
16	78	91
3 K -6		
1	52	48
2	205	217
3	189	200
4	88	-87
5*	35	30
6	142	145
7	157	-169
8	64	60
9*	30	-21
10*	28	-1
11	77	-71
12	34	38
13	70	-73
3 K -7		
5	58	-57
6	106	94
7*	22	-25
8	90	-95
9	109	-120
4 K 0		
1	111	125
2	243	245
3	613	624
4	268	255
5	253	232
6	66	62
7	252	251
8	359	-388
9	449	512
10	117	-95
11	67	-71
12	72	71
13	67	-56
14	302	-329
15	186	-170
16*	37	-5
17	180	-174
18	102	93
19	38	-36
4 K 1		
1	466	-474
2	144	123
3	157	-149
4	300	274
5	591	-606
6	146	133
7	518	517
8	237	236
9	309	317
10	58	51
11	89	-84
12	89	-84
13	433	446
14	54	-46
15	179	174
16	84	-82
17	30	-33
18	50	-56
19	40	-43
4 K 2		
0	374	-380
1	301	-314
2	80	-70
3	265	-273
4	138	-110
5	263	-257
6	47	53
7	385	-432
8	83	68
9	171	-171
10	77	73
11	129	-127
12	281	316
13	74	77
14	127	-126
15	156	187
16*	31	17
17	58	49
18	76	88
4 K 3		
1	287	296
2	227	218
3	370	398
4	330	-368
5	179	-183
6	136	-134
7	162	160
8	56	-48
9	153	-168
10*	43	-6
11	373	-395
12	97	82
13	47	-45
14	61	-54
15	126	-129
16	106	112
17	63	-79
4 K 4		
0*	42	13
1	85	-81
2	197	187
3	60	43
4	49	-34
5	423	436
6	43	-41
7	220	222
8*	42	21
9	41	38
10	181	-177
11	108	97
12*	34	23
13*	30	-24
14	62	-65
4 K 5		
1	219	-198
2	301	309
3	105	-102
4	164	-162
5	84	-79
6	108	101
7	36	39
8	34	32
9	79	78
10*	30	12
11	112	124
12	39	36
13	87	130
4 K 6		
0	56	-49
1	59	-51
2*	31	-4
3	188	-183
4	44	-40
5*	28	-3
6*	27	0
7	88	-74
8	77	94
9	137	-196
4 K -1		
1	564	551
2	604	-589
3	401	361
4	167	149
5	259	-250
6	427	-400
7	182	164
8	143	-134
9	164	-133
10	97	-94
11	520	-572
12	120	-129
13	107	-111
14	246	262
15	46	-45
16*	37	28
17	78	-76
18*	27	16
19	39	43
4 K -2		
0	353	-293
1	142	128
2	402	-357
3*	32	-15
4	94	68
5	755	-775
6	72	58
7	351	-347
8	201	-189
9	115	96
10	268	302
11	175	-184
12	209	225
13	98	78
14*	41	3
15	69	64
16	76	79
17	218	212
4 K -3		
1	278	-272
2	342	-340
3	315	-313
4	559	573
5*	40	-17
6	112	100
7	65	53
8	140	125
9	251	249
10	121	110
11	195	191
12	104	-82
13	108	101
14	142	139
15	118	125
16	151	-147
17*	24	-4
18	102	-151
4 K -4		
0	241	238
1	308	322
2	65	57
3	267	279
4	167	169
5	50	-44
6*	44	19
7	267	278
8	133	-119
9	192	215
10*	43	5
11	58	-44
12	192	-183
13	71	-69
14	41	-41
15	130	-135
16	45	-45
4 K -5		
1	166	165
2	199	-225
3*	43	41
4	85	72
5	233	261
6	114	-108
7	220	-252
8	157	-157
9	137	-133
10*	37	-37
11	53	52
12	44	-44
13	182	-186
14	55	57
4 K -6		
1	76	73
2	73	-77
3	128	-114
4	99	-85
5	165	-168
6	49	-54
7*	34	-18
8	101	93
9	89	-83
10	41	42
11*	23	-9
12	56	-65
5 K 0		
1	91	119
2	130	142
3	225	-215
4	67	59
5	189	-163
6	98	-91
7	234	201
8	188	182
9	83	-74
10	89	83
11*	54	-16
12*	53	-31
13*	50	-4
14*	47	30
15	60	64
16	48	-46
17	127	154
5 K 1		
0	628	-658
1	71	-65
2	310	285
3	135	-111
4	182	140
5	89	66
6	264	-292
7*	54	-10
8	123	109
9	181	-182
10	124	-113
11*	54	-16
12	141	148
13*	48	19
14	51	50
15	39	-21
16	82	[illegible]
5 K 2		
1	119	107
2	192	168
3*	49	22
4*	50	-17
5	60	-53
6	118	-114
7	157	157
8*	54	43
9	55	-93
10	81	96
11*	51	-12
12	155	-171
13*	44	-28
14	60	-56
15	101	-109
16	73	80
5 K 3		
0	230	-235
1	184	166
2	105	101
3	118	-113
4*	53	-11
5	97	87
6	86	-78
7	186	216
8	169	181
9	165	-184
10*	48	-33
11	137	135
12*	41	16
13	64	73
14*	31	34
15	58	-79
5 K 4		
1	113	-103
2	58	56
3*	50	22
4	121	-115
5*	45	-19
6	73	-71
7*	47	-6
8*	45	-45
9*	43	-32
10	106	114
11	61	67
12	39	-41
13	52	74
5 K 5		
0	186	180
1	138	136
2*	42	22
3	125	-127
4	57	-52
5	55	-51
6*	38	0
7	87	88
8*	33	3
9	137	-177
10	35	-46
5 K 6		
1*	27	-12
2	65	67
3	61	73
5 K -1		
0**	411	-532
1	299	-311
2	346	379
3	73	64
4	347	339
5	135	119
6	259	-259
7	163	-144
8*	53	-28
9	175	172
10	110	-97
11*	54	-24
12	106	90
13*	50	31
14	115	-113
15	96	98
16	168	-182
17	41	-54
5 K -2		
1	134	114
2	140	-103
3	208	-177
4	115	-95
5*	50	-24
6	169	-152
7	193	184
8*	56	-34
9*	57	37
10	190	-191
11*	54	-39
12	90	69
13	68	-53
14	92	88
15	45	50
16	85	-90
5 K -3		
0	320	-346
1	279	-259
2	101	-100
3	239	212
4	84	72
5	105	85
6	98	-75
7	217	-218
8*	55	-33
9	248	261
10	175	168
11	138	-127
12	169	159
13	132	-125
14*	39	-7
15	75	69
5 K -4		
1	97	72
2	53	-52
3*	53	-6
4	146	142
5*	54	16
6	254	259
7*	53	-47
8	90	93
9*	51	-17
10	131	-132
11	90	-84
12	142	125
13*	36	-19
14*	31	15
15	56	73
5 K -5		
0	295	322
1	93	-90
2*	50	6
3	76	79
4*	49	43
5	97	-95
6	73	65
7	201	-191
8	146	-151
9	165	167
10*	39	-2
11*	34	-17
12	103	-112
5 K -6		
1*	42	-100
2	180	-171
3*	41	28
4	108	-89
5*	32	24
6*	37	23
7	53	-50
8	102	-109
9	75	70
6 K 0		
1	200	-200
2	40	26
3	353	-362
4*	37	-7
4	046	40°0
6	65	46
7	140	-140
8	66	-50
9	282	-329
10*	42	-9
11	70	-70
12	112	106
13	187	193
14	116	-122
15	85	88
6 K 1		
1	156	188
2	216	209
3	422	440
4	127	-105
5	172	-155
6	62	-47
7*	45	15
8*	45	-4
9	118	-116
10	139	135
11	300	-312
12*	35	6
13	54	-48
14	119	-123
15	100	-131
6 K 2		
0	47	36
2	42	-25
3	48	52
4	84	-77
5	370	388
6	64	53
7	255	271
8*	41	-18
9*	40	-5
10*	37	-43
11	62	61
12	75	74
6 K 3		
1	293	-290
2	209	196
3*	40	-7
4	209	-206
5	108	-93
6	64	56
7*	38	-8
8	52	-53
9	172	170
10*	31	-26
11	132	136
12	44	42
6 K 4		
0	133	115
1	46	-39
2*	35	-11
3	170	-160
4*	34	-25
5	98	-90
6	70	63
7	144	-145
8*	27	16
9	121	-137
10	31	-37
6 K 5		
1	96	91
2	82	75
3	87	89
4	87	-97
5	86	104
6 K -1		
1	307	-314
2*	28	5
3	88	-87
4	130	125
5	286	-323
6	172	-155
7	307	301
8*	44	9
9	196	185
10	178	160
11*	40	4
12	123	-107
13	288	294
14	35	-32
15	65	70
6 K -2		
0	116	-122
1	68	48
2	67	58
3	184	162
4	91	82
5	255	255
6*	44	-20
7	321	301
8	83	-74
9	62	52
10*	42	32
11*	39	-13
12	87	79
13	87	76
14	117	-115
15	141	-169
6 K -3		
1	314	320
2	210	-205
3	42	50
4	228	223
5	78	-71
6	127	-131
7	121	137
8*	42	-8
9	144	-147
10	54	56
11	274	-268
12	138	-133
13	47	-53
14	71	74
6 K -4		
0	138	-142
1	48	32
2	41	29
3	71	-57
4	83	84
5	225	-269
6	66	-78
7	147	-130
8	53	-53
9	50	-45
10	37	37
11	40	-42
12	36	36
6 K -5		
1*	37	-11
2	201	-198
3	281	-265
4	148	144
5*	34	7
6*	33	-9
7	113	99
8*	28	8
9	43	43

Table 4. *Final atomic parameters for* $K_2CS_3.H_2O$

The anisotropic temperature factor is of the form:

$$\exp\left[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+hka^*b^*U_{12}+hla^*c^*U_{13}+klb^*c^*U_{23})\right].$$

The standard deviation referred to the last figure is given in parentheses.

	x	y	z	B
K(1)	0·5867 (3)	0·3006 (1)	0·5661 (2)	3·50 (7) Å^2
K(2)	0·7872 (2)	0·5399 (1)	0·7710 (3)	3·21 (7)
S(1)	0·4921 (3)	0·3176 (1)	0·0639 (3)	3·26 (7)
S(2)	0·3855 (3)	0·1353 (1)	0·4366 (3)	3·08 (7)
S(3)	0·7033 (3)	0·4541 (1)	0·2657 (3)	3·51 (7)
O	0·7936 (10)	0·6433 (4)	0·4439 (9)	4·69 (20)
C	0·6940 (10)	0·3783 (4)	0·0913 (9)	2·48 (18)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K(1)	0·053 (1)	0·047 (1)	0·041 (1)	0·008 (1)	−0·007 (1)	0·003 (1)
K(2)	0·040 (1)	0·036 (1)	0·052 (1)	0·001 (1)	−0·003 (1)	0·004 (1)
S(1)	0·045 (1)	0·041 (1)	0·046 (1)	−0·027 (1)	0·021 (1)	−0·014 (1)
S(2)	0·036 (1)	0·041 (1)	0·046 (1)	−0·001 (1)	0·021 (1)	0·007 (1)
S(3)	0·051 (1)	0·043 (1)	0·049 (1)	−0·018 (1)	0·023 (1)	−0·033 (1)
O	0·069 (4)	0·067 (3)	0·057 (3)	−0·002 (6)	0·043 (5)	−0·016 (5)
C	0·048 (4)	0·027 (3)	0·032 (3)	−0·003 (5)	0·006 (5)	0·007 (4)

Table 3, and the final coordinates and anisotropic vibrational parameters are given in Table 4.

To check the refinement results, a three-dimensional difference Fourier summation was calculated. Good agreement was obtained and the maximum deviations were ±0·5 e.Å^{-3}. No clearly resolved peaks corresponding to the two hydrogen atoms in the structure could be found.

All calculations in this study were made on an IBM 360/50 computer. A summary of the programs in use at this Department will appear in a brief review article (Lindgren, 1970).

Discussion

A projection of the structure of potassium trithiocarbonate monohydrate along the [001] direction is shown in Fig. 2. The packing of the CS_3^{2-} groups with the potassium ions and the water molecules is determined chiefly by the electrostatic interactions and the geometry of the system. Hydrogen bonds O–H...O are not present in the structure since all O–O distances are greater than 5 Å, but there are three O–S distances of 3·312, 3·419 and 3·459 Å (see Table 5), which are possible values for O–H...S interactions (Sletten, Sletten & Jensen, 1969). However, any conclusions concerning the positions of the hydrogen atoms cannot be drawn from the present work, and would certainly require a neutron diffraction study.

Table 5. *Interatomic distances* (Å) *in* $K_2CS_3.H_2O$

Standard deviations are given in parentheses.

The symmetry operation for generating atom 2 from the coordinates listed in Table 4 is given after each distance. All distances less than 4 Å are listed.

Table 5 (*cont.*)

K(1)–O	2·738 (7)	$1-x$	$1-y$	$1-z$
K(1)–S(2)	3·166 (3)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$
K(1)–S(2)	3·207 (2)	x	y	z
K(1)–S(1)	3·240 (3)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$
K(1)–S(1)	3·329 (3)	x	y	z
K(1)–S(3)	3·390 (3)	x	y	z
K(1)–S(1)	3·404 (3)	x	y	$1+z$
K(1)–C	3·463 (6)	x	y	z
K(1)–C	3·631 (6)	x	y	$1+z$
K(2)–O	2·745 (6)	$-1+x$	$-1+y$	$-1+z$
K(2)–S(2)	3·206 (3)	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
K(2)–S(2)	3·222 (3)	$-\frac{1}{2}+x$	$-\frac{1}{2}-y$	$-\frac{1}{2}+z$
K(2)–S(3)	3·475 (4)	$1-x$	$-y$	$-z$
K(2)–S(1)	3·312 (3)	$-x$	$-y$	$-z$
K(2)–S(3)	3·475 (4)	$-x$	$-y$	$-z$
K(2)–C	3·532 (6)	$1-x$	$-y$	$-z$
K(2)–S(3)	3·554 (3)	$-1+x$	$-1+y$	z
K(2)–S(3)	3·590 (3)	$-1+x$	$-1+y$	$-1+z$
K(2)–C	3·721 (7)	$-x$	$-y$	$-z$
K(2)–C	3·800 (7)	$-1+x$	$-1+y$	z
O——S(1)	3·312 (6)	$1+\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
O——S(2)	3·419 (7)	$1+\frac{1}{2}-x$	$\frac{1}{2}+y$	$1+\frac{1}{2}-z$
O——S(3)	3·459 (6)	x	y	z
O——S(1)	3·688 (6)	$1-x$	$1-y$	$1-z$
O——S(1)	3·913 (6)	$1-x$	$1-y$	$-z$
S(1) –S(2)	2·965 (3)	x	y	z
S(1) –S(3)	2·966 (3)	x	y	z
S(2) –S(3)	2·966 (3)	x	y	z

The bond distances and angles within the CS_3^{2-} groups show no significant deviations from the expected values for an sp^2-hybridized carbon atom arrangement (Table 6). The deviations from the best least-squares plane through the atoms S(1), S(2), S(3) and C are negligible, being no greater than 0·002 Å for S(1)–S(3) and −0·006 Å for C. The mean value of 1·712 Å for the C–S bond seems reasonable in comparison with the predicted values of 1·61 Å (double bonds) and 1·81 Å (single bonds) (Pauling, 1960), and in comparison with the bond lengths 1·69–1·77 Å found in $SC(SH)_2$ by Krebs & Gattow (1965). These authors have also given a discussion of the influence of electronic distribution on bond distances in the CS_3-group.

In a previous infrared spectroscopic study of $K_2CS_3.H_2O$ at room temperature (Philippot, 1967) a degeneracy of the ν_3 band into two maxima (880 and

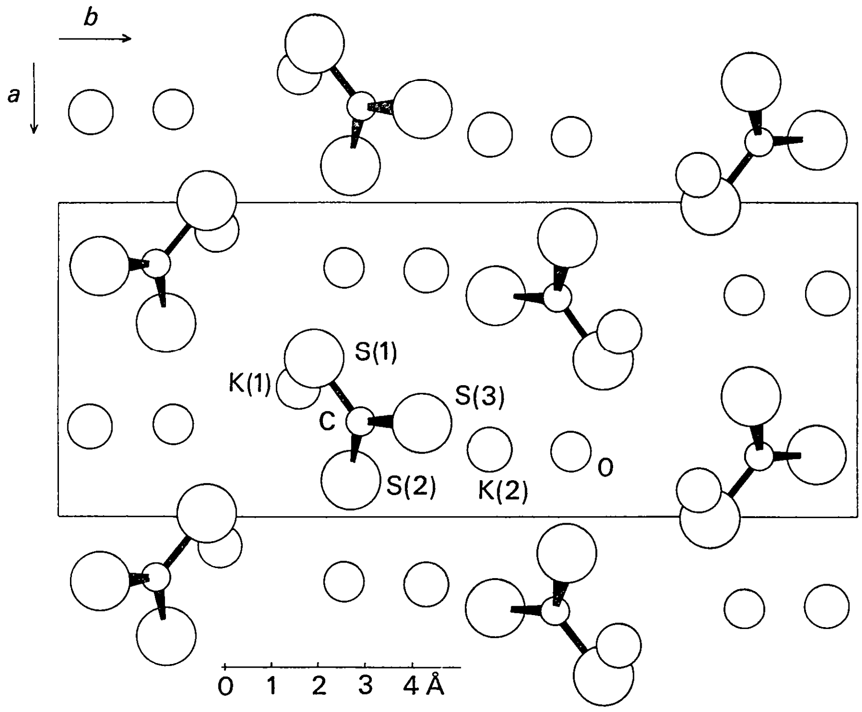

Fig. 2. A projection along the c axis of the structure of $K_2CS_3.H_2O$.

Table 6. *Bond lengths and angles in the* CS_3^{2-} *group*

Standard deviations are given in parentheses.

C–S(1)	1·709 (7) Å	S(1)–C–S(2)	119·7 (4)°
C–S(2)	1·720 (7)	S(1)–C–S(3)	120·4 (4)
C–S(3)	1·708 (6)	S(2)–C–S(3)	119·8 (4)

910 cm^{-1}) has suggested that the CS_3^{2-} ion has a symmetry lower than D_{3h}. The present investigation shows, however, that the CS_3^{2-} ions are planar and regular within the limits of experimental error. A reinvestigation of the infrared spectra at low temperature will therefore be made shortly.

Interatomic distances less than 4 Å are listed in Table 5. The coordination of the potassium ions is sevenfold for K(1) and eightfold for K(2). Each potassium has an oxygen atom at a distance of 2·74 Å and the mean values of the six and seven K–S contact distances are 3·289 and 3·380 Å for K(1) and K(2) respectively, which seems reasonable in comparison with the corresponding value of 3·200 Å for four K–S contacts given in *International Tables for X-ray Crystallography* (1962).

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