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The Crystal Structures of Tetrathioureatellurium(II) Dichloride and Its Dihydrate

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The crystal structures of tetrathioureatellurium(II) dichloride, $Te(tu)_4Cl_2$, and of the dihydrate, $Te(tu)_4Cl_2 \cdot 2H_2O$, have been determined by X-ray methods, and refined by difference syntheses for two projections for each salt. The anhydrous salt is triclinic, $a = 5.83$ Å, $b = 7.77$ Å, $c = 10.86$ Å, $\alpha = 95\frac{1}{2}°$, $\beta = 90°$, $\gamma = 119\frac{1}{2}°$, space group $C_i^1 - P\bar{1}$ with $Z = 1$, while the dihydrate is monoclinic, $a = 6.01$ Å, $b = 16.49$ Å, $c = 9.95$ Å, $\beta = 98\frac{1}{2}°$, space group $C_{2h}^5 - P2_1/c$ with $Z = 2$.

In both salts the tellurium atoms of the $Te(tu)_4^{2+}$ cations lie in centres of symmetry, and are each bonded to four sulphur atoms in a square-planar arrangement, with Te–S bond lengths, 2.69 Å in the anhydrous salt and 2.69 and 2.68 Å in the dihydrate, each ± 0.01 Å. The bonds are thus equal within the error, the average value is 2.685 Å. Within the error the S–Te–S bond angles are 90° in both salts.

The intense yellow colour formed when excess thiourea is added to acid solutions of tetravalent tellurium was apparently first noted by Falciola [1,2] in 1927, and has later been utilized by Vrestal [3-7] and Nielsch [8-11] for the photometric determination of small amounts of tellurium.

From concentrated solutions in the presence of hydrochloric acid, Falciola [1] isolated a yellow, crystalline compound which he tentatively regarded as an addition compound of tellurium tetrachloride and thiourea, but he did not determine its composition. Aynsley and Campbell [12] in 1958 described products obtained from reactions of tellurium tetrachloride and tetrabromide with thiourea, and regarded them as derivatives of tetravalent tellurium. The true nature of the products, as dihalodithioureatellurium(II) compounds and in presence of excess of thiourea, salts of the tetrathioureatellurium(II) cation, was first correctly reported by Vrestal [13-16] in 1957–60 and, independently, by Foss and Hauge [17] in 1959; the latter authors pointed out the square-planar four-coordination of tellurium(II) in these compounds.

Unit cell and space group data have been reported for nine tetrathioureatellurium(II) salts: the anhydrous chloride [18] and bromide, [17,18] which are isomorphous, the chloride dihydrate,[14,17,18] thiocyanate and nitrate,[18] perchlorate,[14,18] fluoride dihydrate and two dimorphs of the hydrogendifluoride.[19] For all of these salts but the perchlorate, the data indicate that the tellurium atoms lie in crystallographic centres of symmetry, from which follows that the TeS_4 grouping is planar.[17-19] The crystal structures of the chloride and its dihydrate are described here.

CRYSTAL DATA

Tetrathioureatellurium(II) dichloride, $Te(tu)_4Cl_2$ (I), occurs as thin, triclinic plates {001} extended along the a axis, with the shorter plate edge parallel to the b axis, and with [18] $a = 5.83$ Å, $b = 7.77$ Å, $c = 10.86$ Å, $\alpha = 95\frac{1}{2}°$, $\beta = 90°$, $\gamma = 119\frac{1}{2}°$. The space group is $C_i^1 - P\bar{1}$ and there is one formula unit per unit cell.

Tetrathioureatellurium(II) dichloride dihydrate, $Te(tu)_4Cl_2 \cdot 2H_2O$ (II), is monoclinic prismatic, and occurs as pseudo-hexagonal prisms extended along the a axis, terminated by {100} and bounded by {010} and {011} and, less developed, by {001}. A drawing of a crystal has been published by Nemec (Ref. 14, p. 36, Fig. 4). The unit cell,[17,18] $a = 6.01$ Å, $b = 16.49$ Å, $c = 9.95$ Å, $\beta = 98\frac{1}{2}°$, contains two formula units, and the space group is $C_{2h}^5 - P2_1/c$. Nemec,[14] from goniometric measurements and rotation photographs, described the crystals as triclinic, his a and b axes are the bc diagonals of the above monoclinic cell.

Intensities were estimated visually from zero-level Weissenberg photographs around the a and b axes of I and the a and c axes of II, taken with Cu$K\alpha$ radiation using a double-film technique. As there turned out to be considerable overlapping in the c-axis projection of II, zero-level photographs around [101] were taken, now integrated, multiple-film; the intensities were estimated photometrically, and the [101] projection instead of the c-axis projection of II was refined. The crystals used were small in order to minimize absorption: prisms with cross-section diameters approximately 0.06, 0.10, and 0.08 mm for the a- and b-axis photographs of I and the a-axis photographs of II, respectively, and an approximate sphere with diameter 0.10 mm for the [101] photographs of II. 150 $0kl$ and 126 $h0l$ reflections of I were recorded with measurable intensities, out of 177 and 139, respectively, accessible with Cu$K\alpha$ radiation, the figures for II were 143 out of 205 $0kl$ reflections and 81 out of 101 $\bar{h}kh$ reflections. Of the 82 non-observed reflections in the $0kl$ and $\bar{h}kh$ zones of II, all but 6 had $k + l$ odd, to these tellurium does not contribute. No absorption corrections were applied (linear absorption coefficients for Cu$K\alpha$ radiation, 220 cm^{-1} for I and 194 cm^{-1} for II). The $\bar{h}kh$ reflections of II were eventually corrected for secondary extinction,[20] with $2g = 1 \times 10^{-5}$.

The calculated structure factors were based on the Thomas-Fermi scattering curve for tellurium, that of Viervoll and Ögrim [21] for sulphur, and those of Berghuis *et al.*[22] for chloride ion, carbon, nitrogen, and oxygen. Calculations were made partly on desk machines, and partly on the IBM 650 computer using Shiono's programs.[23]

THE STRUCTURE ANALYSES

With tellurium in centres of symmetry, the two projections of triclinic I were solved in a straight-forward way through Fourier syntheses including initially about two thirds of the strongest reflections with positive signs. In the case of II, the first Fourier maps, based on the strongest reflections with $k + l$ even, with positive signs, had false symmetry due to the omission of reflections with $k + l$ odd, to which tellurium does not contribute. The correct sulphur and chlorine positions were picked out by a trial and error procedure based on the strongest $k + l$ odd reflections. Refinement of the projections were made through Fourier syntheses and repeated difference syntheses. The carbon and nitrogen positions, which in the presence of tellurium can not be determined with any accuracy, were adjusted on the basis of the known dimensions of the thiourea group in thiourea itself[24] and dichlorobis(thiourea)-zinc.[25]

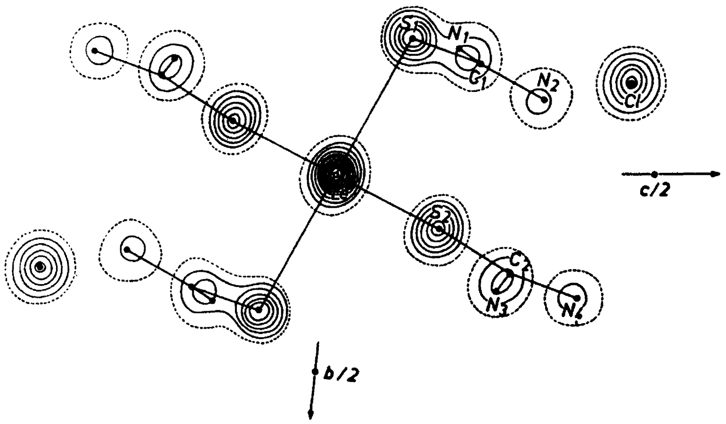

Fig. 1. Electron density projection of anhydrous tetrathioureatellurium(II) dichloride along the a axis. The 4-electron line is dashed. Contour intervals: 10 e.Å^{-2} for tellurium, 4 e.Å^{-2} for the other atoms.

Table 1. Atomic coordinates for tetrathioureatellurium(II) dichloride, in fractions of triclinic cell edges. Origin at a centre of symmetry.

	x	y	z
Te	0	0	0
S_1	−0.205	−0.347	0.0983
C_1	0.052	−0.287	0.208
N_1	0.251	−0.320	0.174
N_2	0.065	−0.190	0.316
S_2	−0.212	0.141	0.1740
C_2	0.028	0.253	0.296
N_3	0.276	0.300	0.277
N_4	−0.028	0.313	0.403
Cl	0.547	−0.233	0.4510

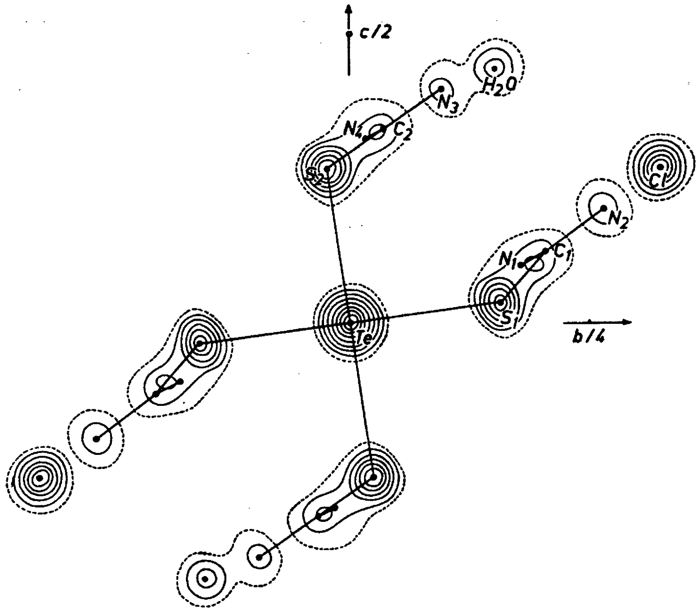

Fig. 2. Electron density projection of tetrathioureatellurium(II) dichloride dihydrate along the *a* axis. The 5-electron line is dashed. Contour intervals: 15 e.$Å^{-2}$ for tellurium, 4 e.$Å^{-2}$ for the other atoms.

The 0*kl* Fourier maps are shown in Figs. 1 and 2. The final atomic coordinates are listed in Tables 1 and 2, and observed and calculated structure factors in Tables 3 and 4.

Table 2. Atomic coordinates for tetrathioureatellurium(II) dichloride dihydrate, in fractions of monoclinic cell edges. Origin at a centre of symmetry.

	x	*y*	*z*
Te	0	0	0
S_1	0.121	0.1565	0.033
C_1	−0.076	0.200	0.122
N_1	−0.285	0.175	0.100
N_2	−0.016	0.265	0.199
S_2	0.102	−0.0245	0.268
C_2	−0.096	0.034	0.333
N_3	−0.021	0.096	0.410
N_4	−0.316	0.015	0.310
Cl	−0.512	0.3240	0.269
H_2O	−0.511	0.151	0.442

Table 3. Observed and calculated $0kl$ and $h0l$ structure factors for tetrathioureatellurium(II) dichloride.

l	F_o	F_c
	$0kl$ zone	
	$00l$	
1	41	+ 43
2	25	+ 26
3	< 4	+ 6
4	26	+ 28
5	30	+ 29
6	32	+ 31
7	43	+ 40
8	< 7	+ 2
9	25	+ 24
10	27	+ 27
11	36	+ 34
12	15	+ 16
13	13	+ 14
	$01l$	
0	39	+ 41
1	50	+ 45
2	46	+ 48
3	70	+ 70
4	42	+ 37
5	61	+ 60
6	32	+ 32
7	37	+ 34
8	15	− 13
9	14	+ 15
10	23	+ 19
11	17	+ 17
12	18	+ 19
13	9	+ 13
	$0\bar{1}l$	
1	33	+ 33
2	24	+ 27
3	< 4	+ 2
4	49	+ 52
5	33	+ 29
6	70	+ 64
7	28	+ 27
8	47	+ 47
9	18	+ 15
10	< 7	+ 3
11	15	+ 13
12	11	+ 9
13	14	+ 14
	$02l$	
0	41	− 41
1	39	+ 40
2	17	− 11
3	38	+ 40
4	44	+ 43
5	48	+ 51
6	29	+ 27
7	12	+ 13
8	38	+ 41
9	27	+ 23
10	24	+ 24
11	9	+ 8
12	8	+ 8
	$0\bar{2}l$	
1	83	+ 88
2	105	+ 105
3	64	+ 59
4	19	+ 17
5	20	+ 17
6	38	+ 37
7	17	+ 16
8	31	+ 31
9	< 7	+ 5
10	< 7	+ 5
11	< 6	+ 5
12	23	+ 26
13	16	+ 18
	$03l$	
0	46	+ 47
1	41	+ 39
2	40	+ 36
3	29	+ 26
4	47	+ 47
5	12	+ 12
6	< 7	+ 4
7	< 7	− 1
8	36	+ 34
9	22	+ 19
10	24	+ 27
11	17	+ 19
12	7	+ 10
	$0\bar{3}l$	
1	54	+ 55
2	39	+ 37
3	41	+ 43
4	11	− 9
5	20	+ 21
6	< 6	− 1
7	37	+ 36
8	24	+ 25
9	25	+ 25
10	24	+ 26
11	12	+ 11
12	13	+ 13
13	< 4	+ 5
	$04l$	
0	23	+ 24
1	< 6	+ 2
2	59	+ 63
3	37	+ 36
4	37	+ 36
5	13	+ 12
6	19	+ 22
7	24	+ 23
8	12	+ 9
9	16	+ 17
10	< 6	+ 3
11	7	+ 8
	$0\bar{4}l$	
1	< 6	− 5
2	< 6	+ 2
3	31	+ 34
4	49	+ 48
5	33	+ 32
6	11	+ 7
7	26	+ 27
8	18	+ 19
9	22	+ 24
10	11	+ 9
11	11	+ 7
12	< 5	− 6
	$05l$	
0	15	+ 13
1	17	+ 15
2	23	+ 22
3	23	+ 21
4	< 7	− 4
5	13	+ 13
6	17	+ 20
7	29	+ 30
8	16	+ 18
9	21	+ 23
10	< 4	+ 4
	$0\bar{5}l$	
1	16	+ 11
2	35	+ 38
3	28	+ 27
4	44	+ 48
5	11	+ 7
6	12	+ 12
7	< 7	− 3
8	< 7	+ 5
9	11	+ 14
10	10	+ 9
11	11	+ 14
	$06l$	
0	23	+ 26
1	38	+ 42

l	F_o	F_c
2	16	+ 11
3	17	+ 18
4	< 7	+ 1
5	12	+ 12
6	10	+ 6
7	9	+ 11
8	11	+ 12
	$0\bar{6}l$	
1	20	+ 17
2	10	+ 8
3	< 7	+ 3
4	< 7	+ 4
5	9	+ 10
6	17	+ 20
7	< 7	+ 4
8	11	+ 11
9	9	+ 9
10	13	+ 20
	$07l$	
0	10	+ 10
1	12	+ 16
2	9	+ 8
3	< 6	+ 6
4	15	+ 19
5	13	+ 14
6	14	+ 17
	$0\bar{7}l$	
1	10	+ 9
2	< 7	− 8
3	11	+ 11
4	9	+ 7
5	20	+ 28
6	16	+ 18
7	9	+ 10
8	< 5	+ 6
9	< 4	+ 1
	$08l$	
0	11	+ 11
1	< 5	+ 1
2	< 5	+ 5
3	< 4	− 3
	$0\bar{8}l$	
1	10	+ 16
2	11	+ 16
3	10	+ 10
4	7	+ 6
5	6	+ 7
6	< 4	+ 1
	$h0l$ zone	
	$00l$	
1	34	+ 43
2	22	+ 26
3	5	+ 6
4	25	+ 28
5	30	+ 31
6	32	+ 33
7	42	+ 43
8	< 6	+ 1
9	23	+ 26
10	28	+ 30
11	38	+ 40
12	17	+ 19
13	15	+ 17
	$10l$	
0	69	+ 72
1	70	+ 77
2	42	+ 37
3	78	+ 96
4	11	+ 12
5	29	+ 31
6	33	+ 32
7	25	+ 21
8	19	+ 16
9	< 6	+ 7
10	32	+ 32
11	11	+ 10
12	28	+ 31
13	20	+ 23
	$\bar{1}0l$	
1	57	+ 59
2	27	− 25
3	20	+ 22
4	35	+ 36
5	36	+ 39
6	36	+ 40
7	25	+ 24
8	36	+ 37
9	19	+ 21
10	43	+ 45
11	14	+ 11
12	12	+ 13
13	< 4	+ 1
	$20l$	
0	27	+ 32
1	13	− 8
2	76	+ 79
3	59	+ 60
4	57	+ 53
5	26	+ 25
6	31	+ 26
7	22	+ 20
8	23	+ 23
9	30	+ 29
10	8	+ 6
11	7	+ 5
12	< 4	+ 7
	$\bar{2}0l$	
1	24	− 15
2	36	+ 33
3	56	+ 50
4	49	+ 45
5	49	+ 45
6	51	+ 14
7	44	+ 42
8	18	+ 14
9	33	+ 37
10	16	+ 16
11	9	+ 3
12	< 5	− 4
13	7	+ 10
	$30l$	
0	15	+ 14
1	11	+ 9
2	8	− 4
3	56	+ 53
4	28	+ 24
5	45	+ 45
6	18	+ 18
7	25	+ 26
8	31	+ 29
9	25	+ 22
10	21	+ 0
11	< 4	0
	$\bar{3}0l$	
1	37	+ 31
2	39	+ 37
3	46	+ 45
4	50	+ 47
5	17	+ 12
6	29	+ 29
7	21	+ 20
8	22	+ 20
9	< 6	− 1
10	14	+ 17
11	5	+ 3
12	9	+ 10
	$40l$	
0	48	+ 50
1	6	− 1
2	11	+ 7
3	< 6	+ 3
4	25	+ 23
5	16	+ 17
6	31	+ 32
7	13	+ 14
8	18	+ 19
9	17	+ 19
10	20	+ 22
	$\bar{4}0l$	
1	50	+ 50

l	F_o	F_c	l	F_o	F_c		F_o	F_c
2	27	+ 28	4	< 6	− 4			
3	22	+ 19	5	20	+ 19		$60l$	
4	8	+ 9	6	10	+ 10	0	6	+ 8
5	26	+ 23	7	13	+ 14	1	17	+ 19
6	8	+ 5	8	< 5	+ 8	2	22	+ 28
7	29	+ 30				3	15	+ 17
8	< 6	− 1		$\bar{5}0l$		4	11	+ 13
9	< 5	+ 3	1	28	+ 29			
10	7	+ 10	2	20	+ 18		$\bar{6}0l$	
11	15	+ 20	3	8	− 8	1	5	+ 6
			4	12	+ 14	2	4	0
	$50l$		5	8	+ 7	3	10	+ 10
0	32	+ 33	6	16	+ 16	4	6	+ 7
1	26	+ 26	7	8	+ 9	5	13	+ 17
2	15	+ 14	8	12	+ 12			
3	19	+ 19	9	6	+ 6			

In the temperature factor exp $[-B(\sin^2\theta/\lambda^2)]$ applied to the calculated structure factors, the final values of B were, in Å² units: In the $0kl$ zone of I, $B = 2.2$ for S_1, 2.8 for S_2 and carbon, 3.2 for chlorine, 2.7 for nitrogen, and $1.8 + 1.5 \cos^2\varphi$ for tellurium, where φ is the angle between the normal of the reflecting plane and the direction of maximum vibration of the atom. This direction made an angle of 16° with the b axis in the acute angle. In the $h0l$ zone of I, $B = 1.7$ for S_1, 2.0 for S_2, 2.5 for chlorine, 2.3 for carbon and nitrogen, and $1.2 + 0.8 \cos^2\varphi$ for tellurium, where the direction of maximum vibration made an angle of 23° with the a axis in the acute angle. In the $0kl$ zone of II, $B = 2.0$ for tellurium and oxygen, and 2.5 for the other atoms; in the $\bar{h}kh$ zone, $B = 1.85$ for tellurium, 2.2 for S_1, 2.4 for S_2, 2.7 for chlorine, 2.3 for carbon, 2.8 for nitrogen, and 3.4 for oxygen.

The reliability index, R, with non-observed reflections included when $|F_c|$ exceeds the observable limit, is 0.084 and 0.096, respectively, for the $0kl$ and $h0l$ zones of I, and 0.096 and 0.082 for the $0kl$ and $\bar{h}kh$ zones of II. The strong reflections, 020, 040, 060, 004, 013, and 033 in the $0kl$ zone and 020 and 040 in the $\bar{h}kh$ zone of II had markedly higher calculated than observed values. They were omitted in the calculation of R indexes, scale factors and difference maps, and were included in the final electron density maps with their calculated instead of observed values.

Slightly different y coordinates were used for the last structure-factor calculations for the two zones of II: $y(S_1) = 0.156$ and 0.1565, $y(C_1) = 0.202$ and 0.200, $y(N_1) = 0.178$ and 0.174, $y(N_2) = 0.265$ and 0.266, $y(S_2) = -0.024$ and -0.025, $y(C_2) = 0.030$ and 0.034, $y(N_3) = 0.095$ and 0.097, $y(N_4) = 0.009$ and 0.016 $y(Cl) = 0.323$ and 0.325, $y(O) = 0.151$ and 0.153, for the $0kl$ and $\bar{h}kh$ zone, respectively. The values of Table 2 are weighted means.

The standard deviations of the atomic coordinates, evaluated from the root-mean-square gradients of the difference maps and the curvature of peaks in the electron density maps, are 0.01 Å or slightly smaller for sulphur and chlorine in both structures, and 0.03—0.04 Å for resolved carbon and nitrogen.

Table 4. Observed and calculated $0kl$ and $\bar{h}kh$ structure factors for tetrathioureatellurium(II) dichloride dihydrate.

k	F_o	F_c
	$0kl$ zone	
	$0k0$	
2	59	+ 78
4	83	+ 102
6	159	+ 212
8	56	+ 59
10	43	+ 44
12	84	+ 90
14	22	+ 17
16	< 16	+ 7
18	32	+ 22
20	16	+ 14
	$0k1$	
1	67	+ 66
2	< 6	+ 5
3	20	+ 15
4	21	− 17
5	100	+ 105
6	43	+ 36
7	75	+ 79
8	23	+ 18
9	27	+ 31
10	< 13	− 1
11	59	+ 58
12	22	+ 20
13	54	+ 50
14	20	+ 10
15	40	+ 41
16	< 16	+ 6
17	34	+ 34
18	26	+ 21
19	35	+ 34
20	< 10	− 8
	$0k2$	
0	27	+ 28
1	28	− 30
2	40	+ 44
3	51	+ 53
4	33	− 23
5	< 9	+ 7
6	59	+ 57
7	12	− 11
8	64	+ 67
9	< 12	+ 6
10	30	+ 25
11	< 14	+ 11
12	54	+ 44
13	< 15	+ 9
14	77	+ 77
15	< 16	+ 4
16	20	+ 18
17	< 15	+ 11
18	39	+ 37
19	< 12	0
20	46	+ 51
	$0k3$	
1	118	+ 174
2	123	− 131
3	103	+ 156
4	64	+ 63
5	85	+ 91
6	29	− 31
7	87	+ 93
8	52	− 53
9	63	+ 67
10	17	+ 15
11	37	+ 34
12	25	− 22
13	60	+ 60
14	29	− 32
15	23	+ 21
16	< 15	+ 15
17	19	+ 19
18	< 13	− 3
19	26	+ 26
20	< 9	+ 3
	$0k4$	
0	116	+ 133
1	13	− 10
2	74	+ 78
3	< 10	+ 1
4	72	+ 77
5	37	+ 32
6	110	+ 117
7	43	− 44
8	54	+ 60
9	< 14	+ 6
10	30	+ 25
11	< 15	+ 8
12	68	+ 60
13	< 16	− 10
14	26	+ 22
15	< 16	+ 3
16	21	+ 21
17	< 14	+ 1
18	25	+ 25
19	< 10	− 5
	$0k5$	
1	50	+ 53
2	< 11	+ 6
3	19	+ 18
4	27	+ 16
5	30	+ 22
6	57	+ 58
7	59	+ 59
8	< 14	+ 6
9	27	+ 23
10	15	+ 15
11	57	+ 51
12	52	+ 49
13	49	+ 45
14	< 15	− 3
15	27	+ 27
16	< 14	− 2
17	32	+ 27
18	21	+ 23
19	29	+ 31
	$0k6$	
0	20	+ 15
1	< 13	+ 3
2	55	+ 64
3	16	− 12
4	60	+ 67
5	20	− 15
6	28	+ 30
7	< 14	+ 6
8	64	+ 67
9	30	− 32
10	35	+ 32
11	< 16	+ 15
12	28	+ 26
13	< 15	− 2
14	47	+ 50
15	< 14	− 17
16	27	+ 27
17	< 11	+ 9
18	25	+ 25
	$0k7$	
1	70	+ 69
2	35	− 35
3	72	+ 66
4	< 14	+ 10
5	51	+ 45
6	< 15	− 5
7	53	+ 49
8	51	− 56
9	54	+ 56
10	< 16	− 1
11	22	+ 20
12	< 15	+ 6
13	33	+ 38
14	20	− 23
15	18	+ 24
16	< 11	− 1
17	< 8	+ 9
	$0k8$	
0	58	+ 51

k	F_o	F_c
1	23	− 21
2	43	+ 41
3	< 15	− 1
4	47	+ 46
5	44	+ 42
6	51	+ 49
7	< 16	0
8	22	+ 17
9	26	+ 17
10	43	+ 43
11	28	+ 26
12	32	+ 24
13	< 13	− 1
14	< 12	+ 10
15	< 10	+ 2
	$0k9$	
1	36	+ 38
2	< 16	+ 1
3	< 16	+ 7
4	< 16	+ 12
5	47	+ 46
6	< 15	+ 12
7	27	+ 30
8	< 15	+ 1
9	< 15	+ 19
10	< 14	− 1
11	38	+ 38
12	22	+ 24
13	21	+ 20
14	< 8	+ 9
	$0k10$	
0	21	+ 19
1	< 15	− 3
2	24	+ 29
3	< 15	− 13
4	32	+ 38
5	< 14	− 7
6	< 14	+ 15
7	< 14	+ 7
8	21	+ 29
9	15	− 23
10	28	+ 35
11	< 10	+ 9
12	17	+ 23
	$0k11$	
1	23	+ 24
2	< 13	− 12
3	40	+ 48
4	< 13	+ 4
5	24	+ 22
6	< 12	− 3
7	21	+ 24
8	< 10	0
9	25	+ 29
10	< 7	+ 6

k	F_o	F_c
	$0k12$	
0	20	+ 25
1	16	− 18
2	25	+ 36
3	11	+ 9
4	23	+ 30
5	16	+ 23
	$\bar{h}kh$ zone	
	$0k0$	
2	46	+ 78
4	71	+ 93
6	224	+ 214
8	47	+ 52
10	38	+ 34
12	84	+ 89
14	17	+ 11
16	< 10	0
18	32	+ 27
20	15	+ 12
	$\bar{1}k1$	
1	99	+ 96
2	28	− 30
3	43	+ 47
4	54	+ 64
5	81	+ 90
6	< 6	+ 2
7	93	+ 111
8	23	+ 26
9	34	+ 37
10	57	+ 62
11	33	+ 31
12	19	− 17
13	70	+ 66
14	33	+ 28
15	38	+ 36
16	25	+ 22
17	17	+ 14
18	< 9	− 6
19	34	+ 36
20	< 6	+ 5
	$\bar{2}k2$	
0	53	+ 48
1	67	+ 68
2	97	+ 106
3	42	+ 43
4	26	+ 29
5	35	− 41
6	53	+ 54
7	55	+ 56
8	72	+ 77
9	31	+ 27
10	38	+ 35
11	< 10	− 15
12	43	+ 42
13	40	+ 32

k	F_o	F_c
14	60	+ 58
15	16	+ 14
16	19	+ 19
17	13	− 15
18	29	+ 28
19	< 7	0
	$\bar{3}k3$	
1	51	+ 50
2	40	+ 41
3	20	+ 18
4	50	− 53
5	52	+ 57
6	< 9	− 8
7	52	+ 54
8	40	+ 45
9	33	+ 31
10	23	− 26
11	51	+ 51
12	< 11	− 7
13	51	+ 50
14	19	+ 14
15	34	+ 30
16	< 9	+ 1
17	45	+ 46
18	< 7	− 3
	$\bar{4}k4$	
0	35	+ 33
1	20	+ 23
2	24	+ 21
3	< 10	+ 1
4	39	+ 40
5	15	− 18
6	28	+ 30
7	18	− 16
8	28	+ 28
9	< 9	0
10	41	+ 41
11	13	− 18
12	33	+ 33
13	9	− 13
14	26	+ 24
15	14	+ 9
16	46	+ 36
17	11	− 12
	$\bar{5}k5$	
1	41	+ 41
2	< 11	− 6
3	71	+ 72
4	< 11	− 16
5	34	+ 34
6	22	− 19
7	27	+ 24
8	12	− 10
9	51	+ 50
10	< 9	− 10

k	F_o	F_c	k	F_o	F_c	k	F_o	F_c
11	25	+ 26	1	< 9	+ 4	8	30	+ 31
12	21	− 23	2	44	+ 46	9	< 6	0
13	11	+ 8	3	< 9	+ 7	10	37	+ 32
14	< 6	− 5	4	44	+ 48			
			5	< 9	− 6			
	$\bar{6}k6$		6	19	+ 18			
0	17	+ 16	7	8	+ 9			

THE TETRATHIOUREATELLURIUM(II) ION

With the tellurium atoms in crystallographic centres of symmetry, the TeS_4 coordination groups are exactly planar. Bond lengths and angles involving the tellurium and sulphur atoms, from the atomic coordinates of Tables 1 and 2, are listed in Table 5, together with their standard deviations. Drawings of the ion in the two salts are reproduced in Fig. 3.

Table 5. Dimensions of the coordination groups.

	Anhydrous salt	Dihydrate
$Te-S_1$	2.685 ± 0.01 Å	2.688 ± 0.01 Å
$Te-S_2$	2.690 ± 0.01	2.677 ± 0.01
$\angle S_1-Te-S_2$	90.6 ± 0.3°	90.3 ± 0.3°
S_1-C_1	1.75 ± 0.06 Å	1.73 ± 0.06 Å
S_2-C_2	1.76 ± 0.06	1.73 ± 0.06
$\angle Te-S_1-C_1$	99.0 ± 2.1°	105.5 ± 2.0°
$\angle Te-S_2-C_2$	105.0 ± 2.0	102.6 ± 1.7

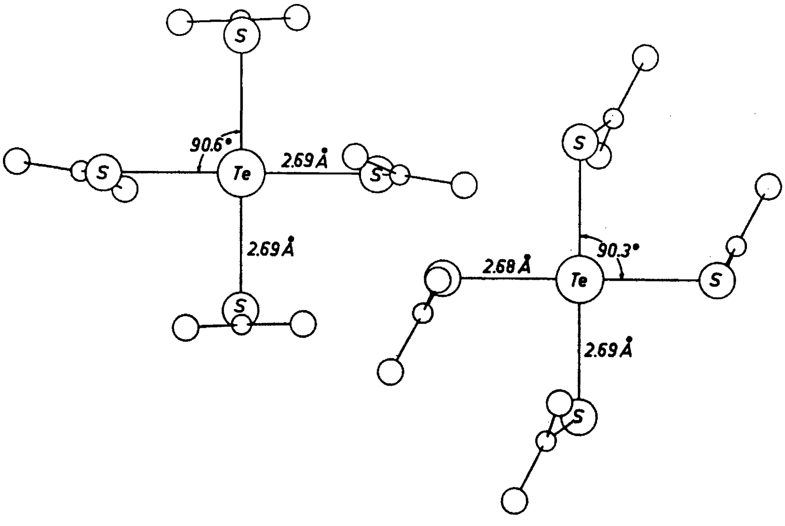

Fig. 3. The tetrathioureatellurium(II) ion, as seen normal to the TeS_4 plane. Left: anhydrous salt; right: dihydrate.

The derived tellurium-sulphur bond lengths are equal within the experimental error: average Te—S = 2.685 Å, which is considerably larger than the sum of the covalent single-bond radii, 2.41 Å. The S—Te—S angles are 90° within the error. Bond lengths in square-planar tellurium(II) complexes have been commented upon in terms of a bonding scheme based on tellurium 5*p* orbitals.[26]

The carbon and nitrogen coordinates give C—N bond lengths of 1.13 to 1.35 Å, S—C—N bond angles 117°—121°, and N—C—N angles 119°—122°, with rather large standard deviations. The thiourea groups are planar within the error, the maximum distance of the middle atom, carbon, from the least-squares planes of the groups, with sulphur given three times the weight of carbon and nitrogen, is 0.05 Å in both salts.

The shape of the complex ion, with respect to the $-C(NH_2)_2$ parts of the thiourea group, depends on the Te—S—C bond angle and the degree of rotation about the Te—S and S—C bonds. The angle between the Te—S—C plane and the TeS_4 plane is 88° for the S_1 thiourea group in the anhydrous salt and 90° for the S_2 group, 67° for the S_1 thiourea group in the dihydrate and 66° for the S_2 group. The angles between the Te—S—C plane and the least-squares planes of the thiourea groups are 87° and 14°, respectively, for the S_1 and S_2 thiourea groups in the anhydrous salt, and 30° and 66° in the dihydrate. Particularly the latter angles vary considerably; however, in both salts the thiourea groups of an ion are nearly parallel, the angle between the least-squares planes of the two non-equivalent groups being 19° in the anhydrous salt and 9° in the dihydrate. The arrangement thus appears to be determined by spatial requirements within the ion, and by packing forces in the crystals.

The shortest tellurium-chlorine distance is 5.59 Å in the anhydrous salt and 4.59 Å in the dihydrate.

THE PACKING IN THE CRYSTALS

The amino hydrogen atoms of the thiourea groups form hydrogen bonds to the chloride ions, as would be expected from hydrogen bonding in other crystals.[27,28] In the dihydrate, the water molecule participates, as hydrogen donor and acceptor. The amino hydrogen atoms are assumed to be located in or not far from positions corresponding to planar trigonal nitrogen, *i. e.*, in or close to the planes of the thiourea groups. The N—H···Cl distances in the present structures are in the normal range, from about 3.2 Å upwards. Examples given by Fuller [28] for $-NH_2$ and $-NH_2^+$ as hydrogen donor to chloride ion range from 3.17 to 3.38 Å. In tris(thiourea)copper(I) chloride,[29] N—H···Cl approaches of 3.24 to 3.44 Å occur; in tetrakis(thioacetamide)copper(I) chloride,[30] the chloride ions, in positions of $\bar{4}$ symmetry, are surrounded by four nitrogen atoms at N—H···Cl = 3.22 Å and ∠C—N···Cl = 115°.

In the *anhydrous salt*, the closest contacts of the N_1 and N_2 atoms of the S_1 thiourea group are with the chloride ions $Cl_A(x,y,z)$ and $Cl_B(x-1,y,z)$, where x,y,z are the Cl coordinates of Table 1. Those of the N_3 and N_4 atoms of the S_2 thiourea group are with the chloride ions $Cl_C(x,1+y,z)$, $Cl_D(1-x,\bar{y},1-z)$, and $Cl_E(\bar{x},\bar{y},1-z)$. Table 6 gives the N···Cl distances and the C—N···Cl angles,

Table 6. Nitrogen-chlorine distances in the anhydrous salt.

Distance	Length N···Cl	Angle C—N···Cl	Distance from plane
$N_1 \cdots Cl_A$	3.31 Å	98°	0.67 Å
$N_2 \cdots Cl_A$	3.34	98	0.67
$N_2 \cdots Cl_B$	3.24	123	1.16
$N_3 \cdots Cl_C$	3.50	94	−2.25
$N_3 \cdots Cl_D$	3.30	100	1.87
$N_4 \cdots Cl_C$	3.46	97	−2.25
$N_4 \cdots Cl_D$	3.56	89	1.87
$N_4 \cdots Cl_E$	3.22	138	0.43

and the distances of the chloride ion from the least-squares plane of the thiourea group. The standard deviations of the N···Cl distances are about 0.05 Å in both salts.

The $N_3,N_4 \cdots Cl_C,Cl_D$ distances are rather large, and the chloride ions lie rather far out of the thiourea plane. However, the midpoint between Cl_C and Cl_D, the symmetry centre at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$, lies on, 0.19 Å out of the plane, 2.70 Å from N_3 and 2.83 Å from N_4, at angles of 99° and 93° with the C—N bonds. With the N_3—H and N_4—H bonds directed not toward Cl_C or Cl_D but toward their midpoint, the symmetry centre, the hydrogen atoms would lie 1.7—1.8 Å from the centre, and 2.6—2.8 Å from the chloride ions. This would be the two "inner" hydrogen atoms of the S_2 thiourea group; of the two "outer" ones, that of N_4 engages toward Cl_E while that of N_3 does not appear to participate in hydrogen bonding, nor does the "outer" hydrogen atom of N_1.

In the *dihydrate*, the chloride ions $Cl_A(x,y,z)$ and $Cl_B(1+x,y,z)$ lie 0.50 and −0.28 Å, respectively, out of the least-squares plane of the S_1 thiourea group, at distances $N_1 \cdots Cl_A = 3.38$ Å, $N_2 \cdots Cl_A = 3.31$ Å, $N_2 \cdots Cl_B = 3.16$ Å, and C—N···Cl angles of 98°, 100°, and 123°, respectively. The chloride ion $Cl_C(x,\frac{1}{2}-y,z-\frac{1}{2})$ lies 3.37 Å from N_1 at a C—N···Cl angle of 114°, but 2.64 Å out of the thiourea plane.

The water oxygen atoms $O_A(x,y,z)$ and $O_B(1+x,y,z)$ lie −0.21 and −0.32 Å, respectively, out of the plane of the S_2 thiourea group, at distances $N_3 \cdots O_A = 3.14$ Å, $N_3 \cdots O_B = 3.17$ Å, $N_4 \cdots O_A = 2.93$ Å, and C—N···O angles of 92°, 121°, and 101°, respectively. The chloride ion $Cl_D(\bar{x}-1,y-\frac{1}{2},\frac{1}{2}-z)$ lies 3.37 Å from N_4, at a C—N···Cl angle of 121°, and 1.21 Å out of the thiourea plane. The chloride ions Cl_A and $Cl_E(x,\frac{1}{2}-y,\frac{1}{2}+z)$ lie 3.33 and 3.28 Å, respectively, from the water oxygen atom, O_A, at a Cl···O···Cl angle of 114° in directions away from the N—H···O contacts; these chloride ions appear to be the acceptors for the water hydrogen atoms.

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REFERENCES

1. Falciola, P. *Ann. Chim. Appl.* **17** (1927) 359; *Chem. Abstr.* **21** (1927) 3580; *Z. anal. Chem.* **75** (1928) 410.
2. Töpelmann, H. *Z. anal. Chem.* **82** (1930) 284.
3. Vrestal, J. *Sb. Celostatni Pracovni Konf. Anal. Chemiku* **1** (1952) 171 (Pub. 1953); **49** (1955) 13019a.

4. Jilek, A. and Vrestal, J. *Chem. Zvesti* **6** (1952) 497; *Chem. Abstr.* **48** (1954) 6315h.
5. Jilek, A. and Vrestal, J. *Chem. Zvesti* **7** (1953) 33; *Chem. Abstr.* **48** (1954) 10484i.
6. Jilek, A. and Vrestal, J. *Chem. Zvesti* **7** (1953) 623; *Chem. Abstr.* **52** (1958) 8827a.
7. Jilek, A., Vrestal, J. and Havir, J. *Chem. Zvesti* **10** (1956) 110; *Chem. Abstr.* **50** (1956) 8388c.
8. Nielsch, W. and Böltz, G. *Z. Metallk.* **45** (1954) 380.
9. Nielsch, W. *Z. anal. Chem.* **144** (1955) 191.
10. Nielsch, W. and Giefer, L. *Z. anal. Chem.* **145** (1955) 347.
11. Nielsch, W. and Giefer, L. *Z. anal. Chem.* **155** (1957) 401.
12. Aynsley, E. E. and Campbell, W. A. *J. Chem. Soc.* **1958** 3290.
13. Vrestal, J. *Conf. Inorg. Chem. Czech. Acad. Sci., Chem. Sect.*, Liblice 1957. Cited from Refs. 14 and 16.
14. Nemec, D. *Prace Brnen. Zakladny Ceskoslov. Akad. Ved.* **30** (1958) 27.
15. Vrestal, J. *Abstr. 17th Intern. Congr. Pure Appl. Chem.*, München, Aug. 30 — Sept. 6, 1959, Vol. 1, p. 135. Verlag Chemie, Weinheim/Bergstr. 1959.
16. Vrestal, J. *Collection Czech. Chem. Commun.* **25** (1960) 443.
17. Foss, O. and Hauge, S. *Acta Chem. Scand.* **13** (1959) 1252.
18. Foss, O. and Hauge, S. *Acta Chem. Scand.* **15** (1961) 1616.
19. Foss, O. and Hauge, S. *Acta Chem. Scand.* **15** (1961) 1623.
20. Bunn, C.W. *Chemical Crystallography*, Oxford University Press 1946, p. 209.
21. Viervoll, H. and Ögrim, O. *Acta Cryst.* **2** (1949) 277.
22. Berghuis, J., Haanappel, I. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. and Veenendaal, A. L. *Acta Cryst.* **8** (1955) 478.
23. Shiono, R. *IBM 650 Programs for Crystallographic Computing*, Technical Reports Nos. 2 and 9, Computation and Data Processing Center, University of Pittsburgh 1957.
24. Kunchur, N. R. and Truter, M. R. *J. Chem. Soc.* **1958** 2551.
25. Kunchur, N. R. and Truter, M. R. *J. Chem. Soc.* **1958** 3478.
26. Foss, O. *Acta Chem. Scand.* **16** (1962) 779.
27. Donohue, J. *J. Phys. Chem.* **56** (1952) 502.
28. Fuller, W. *J. Phys. Chem.* **63** (1959) 1705.
29. Okaya, Y. and Knobler, C. B. *Acta Cryst.* **17** (1964) 928.
30. Truter, M. R. and Rutherford, K. W. *J. Chem. Soc.* **1962** 1748.

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