ACTA CHEMICA SCANDINAVICA 20 (1966) 24–32

The Crystal Structure of Tellurium Bis(dimethyldithiophosphate)

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The crystal structure of tellurium bis(dimethyldithiophosphate) has been determined, and refined by three-dimensional X-ray methods. The crystals are built up of $(CH_3O)_2P(S)-S-Te-S-(S)P(OCH_3)_2$ molecules, with tellurium atoms on twofold symmetry axes. The molecule contains a P–S–Te–S–P chain in the *trans* form, with a STeS/TeSP dihedral angle of 90.7°. Other molecular dimensions are $Te-S_2$ = 2.44 Å, $P-S_2$ = 2.09 Å, $P-S_1$ = 1.92 Å and $\angle S_2-Te-S_2'$ = 98.3°.

The molecules are joined together in layers by weak intermolecular $Te\cdots S_1$ bonds of length 3.31 Å. Each tellurium atom participates in two such bonds at a S–Te–S angle of 85.5°. As these weak bonds are *trans* to, and nearly collinear with the $Te-S_2$ bonds, there is a tendency to square-planar coordination around tellurium.

This structure determination is part of a study of compounds of divalent tellurium and selenium with dithio anions.[1] The main objective is to investigate the configuration around the tellurium and selenium atoms. From analogy with square-planar divalent tellurium complexes studied by Foss *et al.*,[2] and with square-planar nickel(II) complexes with dithio anions, a tendency to square-planar configuration around the central tellurium or selenium atom appeared possible also in compounds of divalent tellurium and selenium with dithio anions.[1]

CRYSTAL DATA

Preparation, and unit cell and space group data for tellurium bis(dimethyldithiophosphate), $Te[(CH_3O)_2PS_2]_2$, have been reported earlier.[1] The crystals are orthorhombic with a = 10.37 Å, b = 11.51 Å, c = 12.56 Å, Z = 4; space group D_{2h}^{14}-$Pbcn$. The accuracy of the cell constants is probably within 0.5 %. The molecules possess, by space group requirements and systematic weak reflections, a twofold axis of symmetry passing through the tellurium atom.

For the structure determination, intensities of $0kl$, $2kl$, $4kl$, $hk0$, $hk1$, and $hk2$ reflections were estimated visually from integrated zero-layer and equi-inclination Weissenberg photographs. Cu*Kα* radiation was used for all layers. The cross-sections of the crystals used were about 0.08 × 0.08 mm^2. The crystals appeared to decompose very slowly with liberation of tellurium when exposed to X-rays for a while; this, however, did not appear to impair the quality of the X-ray photographs. 644 out of 822 accessible reflections with $\sin\theta \leqslant 0.985$ were observed and measured. They were corrected for Lorentz and polarization factors, but no absorption correction was applied to the data.

The least squares refinements were carried out on an IBM 1620 computer, using a program by Mair.[3] The weighting scheme No. 3 in this program, was applied in the refinement.

STRUCTURE ANALYSIS

As the twofold axis through the tellurium atom is parallel to the *b* axis, only the *y* coordinate of this atom is unknown. A Patterson projection along the *c* axis gave this coordinate. Subsequent Fourier refinements of the projections along the *a* and *c* axes and use of a model of the dimethyldithiophosphate anion [4] yielded the positions of the lighter atoms.

Further refinement by $(F_o - F_c)$ syntheses greatly improved the structure and led to entirely new positions for two of the light atoms. At the end, temperature factors were assigned to the different types of atoms.

The observed structure factors from all layers were then brought to a common scale by comparison with the calculated values. All the unobserved reflections were removed from the material. Reflections common to two layers were removed from the data obtained by *a*-axis rotation. These, rather than common reflections from *c*-axis rotation were removed because of the higher observed intensities of the latter. The crystal structure was further refined by means of successive least squares refinements based on the remaining material. Anisotropic temperature factors were used for tellurium, sulphur, and phosphorus. The reflections 002, 020, 023, 221, 404, 110, 310, 112, and 102 which had consistently much higher calculated than observed values, were removed from the data after the fifth cycle, as this effect was attributed to secondary extinction. After this cycle, the observed structure factors for the different layers were rescaled in relation to each other by comparison with the calculated values. After the twelfth and final least squares refinement cycle, the reliability index $R = \sum||F_o|-|F_c||/\sum|F_o|$ had converged to 0.080.

A final structure factor calculation using the parameter output from the last refinement, was then made for all reflections with $\sin\theta \leqslant 0.985$, except the common reflections removed earlier. The R-value for this material with non-observed reflections included only when F_c exceeds the observable limit, is 0.088. The final observed and calculated structure factors are listed in Table 1. The calculated values are based on atomic scattering factors for tellurium by Thomas and Umeda,[5] for sulphur by Dawson,[6] for phosphorus by Freeman and Watson,[7] and for oxygen and carbon by Hoerni and Ibers.[8]

Table 1. Observed and calculated 0*kl*, 2*kl*, 4*kl*, *hk*0, *hk*l and *hk*2 structure factors for tellurium bis(dimethyldithiophosphate). The absolute values are multiplied by a factor of five.

H	K	L	FO	FC
0	0	2	1152	-1728
0	0	4	377	- 267
0	0	6	435	- 411
0	0	8	598	596
0	0	10	120	91
0	0	12	148	- 153
0	0	14	261	- 280
0	2	3	944	1100
0	2	4	163	86
0	2	5	965	-1042
0	2	6	289	270
0	2	7	565	499
0	2	8	189	- 156
0	2	9	483	- 461
0	2	10	80	64
0	2	11	470	500
0	2	12	165	- 144
0	2	13	224	- 226
0	2	14	< 76	40
0	2	15	< 67	11
0	4	3	257	- 202
0	4	4	699	- 716
0	4	5	321	- 265
0	4	6	641	635
0	4	7	555	598
0	4	8	355	- 320
0	4	9	274	- 249
0	4	10	251	219
0	4	11	< 82	55
0	4	12	331	- 327
0	4	13	129	- 149
0	4	14	218	222
0	4	15	< 57	21
0	6	3	357	- 308
0	6	4	680	- 692
0	6	5	178	158
0	6	6	< 73	- 24
0	6	7	415	- 439
0	6	8	337	312
0	6	9	299	292
0	6	10	< 82	44
0	6	11	< 79	5
0	6	12	172	- 167
0	6	13	71	45
0	6	14	< 61	27
0	8	3	< 75	- 2
0	8	4	449	437
0	8	5	< 79	32
0	8	6	431	- 408
0	8	7	359	- 374
0	8	8	407	401
0	8	9	204	210
0	8	10	409	- 434
0	8	11	69	56
0	8	12	239	246
0	8	13	< 56	8
0	10	3	250	194
0	10	4	166	136
0	10	5	285	- 238
0	10	6	285	- 289
0	10	7	254	226
0	10	8	336	340
0	10	9	< 76	- 30
0	10	10	245	- 234
0	10	11	< 60	36
0	12	3	398	368
0	12	4	264	- 216
0	12	5	294	- 275
0	12	6	91	52
0	12	7	< 68	- 19
0	12	8	60	- 39
0	12	9	65	40
0	14	3	< 58	5
0	14	4	< 52	10
2	0	4	674	700
2	0	6	897	- 906
2	0	8	831	857
2	0	10	566	- 609
2	0	12	296	308
2	0	14	115	- 106
2	1	3	161	121
2	1	4	161	- 169
2	1	5	286	278
2	1	6	398	364
2	1	7	< 74	- 44
2	1	8	306	- 261
2	1	9	189	- 156
2	1	10	123	- 134
2	1	11	< 95	- 44
2	1	12	203	215
2	1	13	106	110
2	1	14	< 87	- 2
2	1	15	< 77	29
2	2	3	695	791
2	2	4	188	- 151
2	2	5	484	- 497
2	2	6	276	- 271
2	2	7	389	386
2	2	8	428	430
2	2	9	252	- 212
2	2	10	267	- 233
2	2	11	200	157
2	2	12	< 94	42
2	2	13	217	- 210
2	2	14	< 85	13
2	2	15	169	199
2	3	3	341	- 303
2	3	4	231	- 217
2	3	5	147	- 153
2	3	6	613	647
2	3	7	129	118
2	3	8	< 85	70
2	3	9	124	122
2	3	10	314	- 321
2	3	11	95	- 102
2	3	12	< 93	- 27
2	3	13	< 91	- 14
2	3	14	98	88
2	3	15	< 69	5
2	4	3	496	493
2	4	4	655	- 675
2	4	5	206	- 167
2	4	6	532	542
2	4	7	205	- 179
2	4	8	359	- 344
2	4	9	240	190
2	4	10	272	245
2	4	11	< 95	- 20
2	4	12	211	- 220
2	4	13	90	- 77
2	4	14	156	160
2	4	15	93	101
2	5	3	333	- 290
2	5	4	117	120
2	5	5	290	- 291
2	5	6	< 81	- 36
2	5	7	207	183
2	5	8	< 91	- 46
2	5	9	206	183
2	5	10	< 95	- 40
2	5	11	124	- 109
2	5	12	< 92	67
2	5	13	< 88	- 51
2	5	14	< 77	50
2	6	3	397	- 380
2	6	4	188	- 162
2	6	5	468	465
2	6	6	348	338
2	6	7	518	- 525
2	6	8	312	- 323
2	6	9	457	461
2	6	10	214	196
2	6	11	281	- 300
2	6	12	151	- 118
2	6	13	159	140
2	6	14	< 66	49
2	7	3	< 82	48
2	7	4	199	171
2	7	5	122	95
2	7	6	< 91	- 51
2	7	7	133	116
2	7	8	< 95	25
2	7	9	119	- 120
2	7	10	< 92	- 48
2	7	11	139	- 136
2	7	12	< 85	- 34
2	7	13	100	97
2	8	3	225	- 188
2	8	4	335	284
2	8	5	206	173
2	8	6	220	- 192
2	8	7	236	- 231
2	8	8	154	116
2	8	9	208	213
2	8	10	< 91	- 19
2	8	11	135	- 123
2	8	12	78	44
2	8	13	67	64
2	9	3	205	- 158
2	9	4	95	77
2	9	5	228	- 200
2	9	6	< 95	22
2	9	7	192	167
2	9	8	100	114
2	9	9	130	118
2	9	10	< 86	- 44
2	9	11	127	- 110
2	9	12	100	- 126
2	10	3	305	273
2	10	4	286	253
2	10	5	317	- 294
2	10	6	147	- 128
2	10	7	225	192
2	10	8	< 88	26
2	10	9	182	- 157
2	10	10	< 81	- 3
2	10	11	147	- 155
2	11	3	151	- 126
2	11	4	102	92
2	11	5	143	- 131
2	11	6	190	- 184
2	11	7	88	73
2	11	8	< 84	- 24
2	11	9	106	95
2	11	10	77	89
2	12	3	148	124
2	12	4	137	- 110
2	12	5	198	- 189
2	12	6	159	142
2	12	7	216	228
2	12	8	160	- 153
2	13	3	< 80	- 29
2	13	4	< 78	- 13
2	13	5	74	61
2	13	6	< 67	0
2	13	7	< 52	19
2	14	3	128	- 108
2	14	4	131	- 150
4	0	4	1034	1207
4	0	6	323	- 303
4	0	8	147	- 75
4	0	10	329	- 310
4	0	12	351	392
4	0	14	144	- 148
4	1	3	208	- 190
4	1	4	300	272
4	1	5	139	- 116
4	1	6	< 74	- 43
4	1	7	< 82	15
4	1	8	< 89	43
4	1	9	111	113
4	1	10	< 99	- 53
4	1	11	< 99	- 0
4	1	12	< 95	- 99
4	1	13	< 93	- 70
4	1	14	139	192
4	1	15	< 64	21
4	2	3	303	284
4	2	4	239	217
4	2	5	534	- 546
4	2	6	118	- 97
4	2	7	778	843
4	2	8	203	- 151
4	2	9	537	- 567
4	2	10	192	144
4	2	11	229	232
4	2	12	103	95
4	2	13	192	- 186
4	2	14	144	- 143
4	2	15	115	131
4	3	3	161	- 162
4	3	4	184	168
4	3	5	< 73	59
4	3	6	< 80	- 69
4	3	7	< 86	- 57
4	3	8	< 93	6
4	3	9	< 97	61
4	3	10	< 99	- 30
4	3	11	< 98	19
4	3	12	< 92	- 16
4	3	13	82	- 94
4	3	14	85	96
4	4	3	105	107
4	4	4	453	- 424
4	4	5	193	- 184
4	4	6	409	373
4	4	7	241	227
4	4	8	460	- 468
4	4	9	394	- 415
4	4	10	355	369
4	4	11	278	287
4	4	12	132	- 130
4	4	13	< 87	35
4	4	14	< 75	75
4	5	3	175	- 156
4	5	4	< 80	- 48
4	5	5	174	138
4	5	6	226	220
4	5	7	< 94	- 31
4	5	8	< 97	27
4	5	9	< 99	- 2
4	5	10	98	- 118
4	5	11	< 93	21
4	5	12	< 92	- 0
4	5	13	< 82	- 105
4	5	14	< 65	17
4	6	3	745	- 735
4	6	4	133	78
4	6	5	537	518
4	6	6	218	192
4	6	7	103	- 74
4	6	8	255	- 258
4	6	9	< 99	5
4	6	10	< 96	- 6
4	6	11	181	- 176
4	6	12	< 88	14
4	6	13	168	185
4	7	3	254	- 209
4	7	4	162	- 139
4	7	5	< 95	- 2
4	7	6	166	155
4	7	7	< 99	45
4	7	8	< 99	- 65
4	7	9	< 96	42
4	7	10	< 91	- 36
4	7	11	< 86	3
4	7	12	< 83	73
4	7	13	< 62	- 98
4	8	3	458	- 435
4	8	4	287	250
4	8	5	358	345
4	8	6	402	- 385
4	8	7	< 99	- 3
4	8	8	332	336
4	8	9	< 92	27
4	8	10	182	- 164
4	8	11	160	- 164
4	8	12	120	124
4	9	3	< 99	- 53
4	9	4	143	- 139
4	9	5	< 99	27
4	9	6	105	96
4	9	7	< 95	35
4	9	8	93	- 88
4	9	9	< 91	- 15
4	9	10	< 84	- 10
4	9	11	< 73	- 31
4	10	3	333	307
4	10	4	215	194
4	10	5	155	- 127
4	10	6	209	- 202
4	10	7	< 92	58
4	10	8	197	188

H	K	L	FO	FC
4	10	9	169	- 159
4	10	10	158	- 166
4	11	3	< 93	- 25
4	11	4	115	- 106
4	11	5	105	- 94
4	11	6	110	100
4	11	7	87	76
4	11	8	< 80	- 1
4	11	9	< 65	40
4	12	3	155	132
4	12	4	124	- 104
4	12	5	86	- 65
4	12	6	154	158
4	12	7	143	151
4	13	3	< 78	12
4	13	4	< 73	- 13
4	13	5	100	- 122
0	2	0	879	1027
0	4	0	737	- 718
0	6	0	219	- 184
0	8	0	183	- 130
0	10	0	108	100
0	12	0	151	- 141
0	14	0	245	- 285
1	1	0	521	608
1	3	0	186	119
1	5	0	450	- 433
1	7	0	359	340
1	9	0	576	613
1	11	0	86	- 74
1	13	0	229	- 246
2	0	0	202	163
2	2	0	69	- 65
2	4	0	649	- 668
2	6	0	74	- 69
2	8	0	736	785
2	10	0	399	391
2	12	0	140	- 153
2	14	0	158	- 181
3	1	0	976	1112
3	3	0	591	- 601
3	5	0	643	- 639
3	7	0	144	- 119
3	9	0	119	91
3	11	0	< 57	40
3	13	0	192	- 205
4	0	0	349	318
4	2	0	129	111
4	4	0	715	- 754
4	6	0	661	- 647
4	8	0	355	345
4	10	0	153	159
4	12	0	229	- 230
5	1	0	75	27
5	3	0	927	- 984
5	5	0	587	- 568
5	7	0	266	219
5	9	0	428	417
5	11	0	162	182
5	13	0	143	- 144
6	0	0	376	342
6	2	0	283	- 265
6	4	0	655	- 636
6	6	0	196	- 166
6	8	0	245	209
6	10	0	235	221
6	12	0	82	- 83
7	1	0	503	493
7	3	0	< 52	1
7	5	0	674	- 697
7	7	0	< 58	- 38
7	9	0	295	316
7	11	0	167	- 162
8	0	0	711	763
8	2	0	134	110
8	4	0	411	- 384
8	6	0	< 58	- 21
8	8	0	172	181
8	10	0	133	145
9	1	0	314	328
9	3	0	179	- 151
9	5	0	194	- 172
9	7	0	233	213
9	9	0	377	382
10	0	0	531	542
10	2	0	296	304
10	4	0	180	- 162
10	6	0	79	- 97
10	8	0	257	242
11	1	0	494	537
11	3	0	81	- 89
11	5	0	174	- 149
11	7	0	< 36	20
12	0	0	141	129
12	2	0	< 44	15
12	4	0	237	- 229
12	6	0	97	- 105
13	1	0	56	54
0	2	1	233	- 196
0	4	1	154	- 111
0	6	1	994	1092
0	8	1	579	596
0	10	1	342	- 353
0	12	1	152	- 156
0	14	1	61	76
1	1	1	551	- 678
1	2	1	162	123
1	3	1	453	- 454
1	4	1	75	- 68
1	5	1	537	533
1	6	1	241	219
1	7	1	531	528
1	8	1	246	224
1	9	1	100	79
1	10	1	< 59	- 4
1	11	1	186	- 196
1	12	1	< 55	48
1	13	1	< 52	- 21
1	14	1	< 45	2
2	1	1	254	- 266
2	2	1	1119	-1418
2	3	1	363	322
2	4	1	507	- 508
2	5	1	371	354
2	6	1	344	357
2	7	1	140	- 124
2	8	1	289	290
2	9	1	197	184
2	10	1	132	- 120
2	11	1	156	150
2	12	1	110	- 119
2	13	1	< 52	- 13
2	14	1	139	180
3	1	1	381	- 378
3	2	1	184	168
3	3	1	596	- 637
3	4	1	152	- 141
3	5	1	217	198
3	6	1	211	157
3	7	1	580	602
3	8	1	200	180
3	9	1	143	- 126
3	10	1	< 59	10
3	11	1	337	- 378
3	12	1	102	115
3	13	1	70	- 56
3	14	1	58	83
4	1	1	263	232
4	2	1	552	- 565
4	3	1	141	121
4	4	1	318	262
4	5	1	63	57
4	6	1	536	525
4	7	1	175	157
4	8	1	106	60
4	9	1	< 59	18
4	10	1	317	- 337
4	11	1	< 56	48
4	12	1	326	- 377
4	13	1	< 48	36
5	1	1	523	- 524
5	2	1	220	- 213
5	3	1	878	-1011
5	4	1	252	216
5	5	1	312	- 259
5	6	1	< 52	- 10
5	7	1	310	289
5	8	1	< 58	- 33
5	9	1	172	- 155
5	10	1	89	89
5	11	1	273	- 295
5	12	1	82	- 89
5	13	1	< 44	30
6	1	1	114	79
6	2	1	673	- 722
6	3	1	169	- 136
6	4	1	487	- 469
6	5	1	288	- 261
6	6	1	259	243
6	7	1	< 58	- 48
6	8	1	133	113
6	9	1	117	- 101
6	10	1	234	- 265
6	11	1	64	- 51
6	12	1	113	- 140
6	13	1	< 33	56
7	1	1	384	- 408
7	2	1	87	- 67
7	3	1	144	- 124
7	4	1	< 55	- 31
7	5	1	540	541
7	6	1	146	- 114
7	7	1	371	360
7	8	1	163	- 157
7	9	1	< 56	- 23
7	10	1	54	- 62
7	11	1	296	- 334
7	12	1	52	- 50
8	1	1	81	- 57
8	2	1	389	- 380
8	3	1	< 57	0
8	4	1	225	- 199
8	5	1	< 59	5
8	6	1	349	345
8	7	1	81	- 79
8	8	1	229	235
8	9	1	62	- 39
8	10	1	178	- 167
8	11	1	89	- 85
9	1	1	341	- 334
9	2	1	89	70
9	3	1	491	- 478
9	4	1	195	- 191
9	5	1	72	69
9	6	1	64	- 45
9	7	1	298	304
9	8	1	< 55	- 5
9	9	1	61	39
9	10	1	65	- 76
10	1	1	96	- 88
10	2	1	266	- 267
10	3	1	< 57	- 18
10	4	1	142	116
10	5	1	57	40
10	6	1	394	408
10	7	1	54	- 62
10	8	1	220	230
10	9	1	< 41	18
11	1	1	130	- 111
11	2	1	91	67
11	3	1	163	- 162
11	4	1	107	109
11	5	1	196	184
11	6	1	64	46
11	7	1	300	353
11	8	1	53	54
12	1	1	58	58
12	2	1	361	- 367
12	3	1	< 50	27
12	4	1	127	- 112
12	5	1	42	41
12	6	1	120	134
13	1	1	148	- 169
13	2	1	< 34	- 23
0	2	2	670	- 732
0	4	2	634	677
0	6	2	589	584
0	8	2	149	- 134
0	10	2	96	- 82
0	12	2	192	222
0	14	2	96	113
1	0	2	708	- 908
1	1	2	455	- 564
1	2	2	415	- 401
1	3	2	557	564
1	4	2	177	- 186
1	5	2	551	553
1	6	2	219	- 179
1	7	2	255	- 245
1	8	2	205	191
1	9	2	444	- 465
1	10	2	129	127
1	11	2	68	- 48
1	12	2	< 64	32
1	13	2	165	228
1	14	2	60	80
2	0	2	352	- 343
2	1	2	131	109
2	2	2	244	221
2	3	2	753	- 792
2	4	2	638	682
2	5	2	62	- 62
2	6	2	77	55
2	7	2	182	- 181
2	8	2	541	- 576
2	9	2	252	- 259
2	10	2	337	- 351
2	11	2	142	136
2	12	2	117	126
2	13	2	< 61	4
2	14	2	124	177
3	0	2	904	- 920
3	1	2	861	- 951
3	2	2	186	- 182
3	3	2	217	203
3	4	2	72	- 23
3	5	2	688	709
3	6	2	294	- 252
3	7	2	102	52
3	8	2	< 65	- 9
3	9	2	282	- 278
3	10	2	95	- 105
3	11	2	< 67	64
3	12	2	68	- 85
3	13	2	154	194
3	14	2	62	94
4	0	2	908	- 963
4	1	2	377	- 372
4	2	2	188	- 155
4	3	2	168	- 136
4	4	2	648	643
4	5	2	289	- 282
4	6	2	317	253
4	7	2	82	56
4	8	2	268	- 260
4	9	2	191	175
4	10	2	177	- 170
4	11	2	< 65	24
4	12	2	142	149
4	13	2	< 55	51
5	0	2	401	381
5	1	2	267	- 252
5	2	2	162	- 135
5	3	2	455	430
5	4	2	73	- 64
5	5	2	460	452
5	6	2	199	161
5	7	2	250	- 227
5	8	2	176	- 168
5	9	2	439	- 466
5	10	2	< 67	43
5	11	2	79	- 75
5	12	2	95	101
5	13	2	143	174
6	0	2	534	- 534
6	1	2	234	215
6	2	2	90	- 62
6	3	2	417	371
6	4	2	534	517
6	5	2	< 63	15
6	6	2	236	201
6	7	2	< 68	- 20
6	8	2	344	- 333
6	9	2	< 68	42
6	10	2	214	- 204
6	11	2	140	- 143
6	12	2	114	123
7	0	2	346	313
7	1	2	552	- 558
7	2	2	224	192
7	3	2	257	226
7	4	2	176	153
7	5	2	430	402
7	6	2	200	195
7	7	2	< 69	- 20
7	8	2	< 68	41
7	9	2	179	- 179
7	10	2	< 65	- 30
7	11	2	< 58	36
7	12	2	< 45	- 13
8	0	2	489	- 502
8	1	2	187	152
8	2	2	139	- 106
8	3	2	102	73
8	4	2	411	405
8	5	2	187	168
8	6	2	225	196

H	K	L	FO	FC
8	7	2	83	90
8	8	2	240	-254
8	9	2	< 65	51
8	10	2	161	-172
8	11	2	73	72
9	0	2	< 69	4
9	1	2	204	-184
9	2	2	229	226
9	3	2	300	264
9	4	2	87	74
9	5	2	302	288
9	6	2	117	-118
9	7	2	176	-162
9	8	2	137	110
9	9	2	291	-309
9	10	2	< 49	-9
10	0	2	411	-428
10	1	2	93	84
10	2	2	105	-79
10	3	2	85	-75
10	4	2	294	294
10	5	2	87	60
10	6	2	132	114
10	7	2	< 62	-23
10	8	2	165	-152
10	9	2	115	-126
11	0	2	166	-140
11	1	2	352	-342
11	2	2	173	-172
11	3	2	105	90
11	4	2	115	-98
11	5	2	275	277
11	6	2	57	-23
11	7	2	< 51	6
12	0	2	181	-188
12	1	2	193	-202
12	2	2	< 59	26
12	3	2	97	-85
12	4	2	244	248
12	5	2	109	-128
13	0	2	< 42	30
13	1	2	115	-136
13	2	2	49	-65

Table 2. Final atomic coordinates for tellurium bis(dimethyldithiophosphate), in fractions of cell edges. Origin at a centre of symmetry.

	x	y	z
Te	0.5000	0.6131	0.2500
S_1	0.8636	0.3240	0.1112
S_2	0.6026	0.4744	0.1298
P	0.7852	0.4450	0.1945
O_1	0.8573	0.5644	0.1985
O_2	0.7654	0.4207	0.3183
C_1	0.9243	0.6062	0.1095
C_2	0.7102	0.3191	0.3685

Table 3. Final temperature parameters $\beta_{ij} \times 10^3$. The expression used is exp $-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + kl\beta_{23} + hl\beta_{13} + hk\beta_{12})$.

	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
Te	4.14	4.84	5.66	0.00	−1.37	0.00
S_1	7.93	5.08	4.30	−1.68	−1.97	−3.80
S_2	4.07	5.92	3.59	−1.40	−0.41	−0.23
P	4.52	4.19	1.62	−0.50	−1.09	1.29

For the carbon and oxygen atoms, a temperature factor exp $-B(\sin^2\theta/\lambda^2)$ was used, with $B = 2.96$, 3.92, 3.84 and 3.71 for O_1, O_2, C_1, and C_2, respectively.

The atomic parameter output from the final least squares refinement is listed in Tables 2 and 3.

STRUCTURE OF TELLURIUM BIS(DIMETHYLDITHIOPHOSPHATE) AND THE CONFIGURATION AROUND TELLURIUM

The crystals are built up of tellurium bis(dimethyldithiophosphate) molecules, with the tellurium atoms located on the twofold symmetry axes which run through the crystals parallel to the *b* axis. The molecules are connected through weak, intermolecular Te···S_1 bonds, to form two-dimensional polymeric layers. The bond lengths and angles in the molecule, calculated from the coordinates of Table 2, are listed in Table 4 together with the calculated standard deviations. The uncertainties in cell edges add to the quoted standard deviations. Other interatomic distances and angles are included in this table.

Table 4. Bond lengths and angles.

$Te-S_2$	2.440 ± 0.005 Å	$\angle S_2'-Te-S_2$	$98.3 \pm 0.3°$
$P-S_2$	2.089 ± 0.007	$\angle Te-S_2-P$	105.1 ± 0.3
$P-S_1$	1.923 ± 0.007	$\angle S_2-P-S_1$	106.8 ± 0.3
$P-O_1$	1.57 ± 0.02	$\angle S_2-P-O_1$	107.6 ± 0.6
$P-O_2$	1.59 ± 0.02	$\angle S_2-P-O_2$	106.9 ± 0.7
O_1-C_1	1.40 ± 0.03	$\angle S_1-P-O_1$	116.9 ± 0.6
O_2-C_2	1.45 ± 0.03	$\angle S_1-P-O_2$	117.3 ± 0.6
		$\angle P-O_1-C_1$	120.8 ± 1.4
		$\angle P-O_2-C_2$	128.2 ± 1.4
		$\angle O_1-P-O_2$	100.6 ± 0.8

Other interatomic distances and angles.

S_1-O_1	2.98 ± 0.02 Å	$\angle S_2-Te-S_1'(I)$	$88.1 \pm 0.3°$
S_1-O_2	3.01 ± 0.02	$\angle S_2-Te-S_1(II)$	173.0 ± 0.3
S_2-O_1	2.97 ± 0.02	$\angle S_1(I)-Te-S_1(II)$	85.5 ± 0.3
S_2-O_2	2.97 ± 0.02	$\angle P'(I)-S_1'(I)-Te$	115.2 ± 0.3
$P-C_1$	2.43 ± 0.03		
$P-C_2$	2.58 ± 0.03		
O_1-O_2	2.74 ± 0.02		
$Te-S_1'(I)$	3.306 ± 0.005		

I and II denote molecules generated from the one in Table 1 by a centre of symmetry in $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and then by twofold screw axes parallel with c through $(\frac{3}{4},\frac{3}{4})$ and $(\frac{1}{4},\frac{3}{4})$ in Fig. 2, respectively.

The P—S—Te—S—P chain has a *trans* configuration. Both *cis* and *trans* configurations have been reported for pentathionic compounds.[9]

The molecule, seen along the normal to the least-squares plane through the tellurium atom and the four closest sulphur atoms with tellurium given triple weight, is shown in Fig. 1. Based on atomic coordinates in Å units, this plane has the equation $0.7927x-0.6096z + 1.9142 = 0$. Two of the four closest sulphur atoms belong to the molecule proper, and the other two, more weakly bonded ones, belong to two different neighbouring molecules. The two sulphur atoms closest to tellurium are 0.08 Å on each side of this plane, and the other two are 0.05 Å on each side, with the tellurium atom exactly in the plane. The S—Te—S angles are all near 90 or 180° as shown in Fig. 1. Thus this compound might be considered a distorted square-planar complex of divalent tellurium. In the plane, the short Te—S bonds are *cis* to each other, but *trans* to and nearly collinear with the long ones. This effect is found in square-planar *cis* tellurium(II) complexes, where a thiourea sulphur atom bonded to tellurium has a pronounced lengthening effect on the tellurium-halogen bond *trans* to it.[2] If in these compounds, the Te—S and Te—X bonding occur mainly through overlap of atomic *p*-orbitals in the bond direction[2] as proposed for trihalides and related compounds,[10,11] this type of bonding should lead to lengthening of the bonds involved, relative to single, covalent bonds. Using a "half *p*-bond" radius of 1.64 Å for tellurium,[2] the S—Te···S system, if symmetrical would be expected to have a total length of about 5.36 Å which is equal to the corresponding length found in symmetrical square-planar *trans* tellurium(II) complexes.[2] Table 4 actually yields a distance

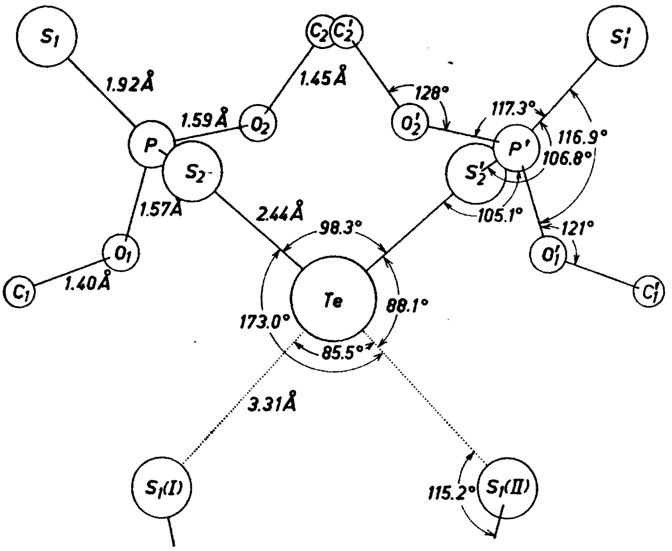

Fig. 1. The tellurium bis(dimethyldithiophosphate) molecule, and the configuration around the tellurium atom, seen along the normal to the least squares plane through the tellurium atom and the four closest sulphur atoms.

of 5.75 Å, but then, the asymmetry is rather pronounced. Similar asymmetry has earlier been found in connection with extra long three-atomic systems of this type.[2,12]

The intramolecular Te—S bond of 2.44 Å is a little longer than a single covalent bond of 2.41 Å or the Te—S bonds of about 2.35 Å found in some telluropentathionic compounds.[9] The weak intermolecular Te···S bond has a length of 3.31 Å which is considerably shorter than the sum of van der Waals radii, which according to Pauling [13] is 4.05 Å.

In the dimethyldithiophosphate group, there are two significantly different P—S bonds, of lengths 2.09 Å and 1.92 Å. The sulphur atoms in these bonds participate in the short and long Te—S bonds, respectively. The long P—S bond has the same length as the P—S single bond found in various phosphorus sulphides.[14] The short P—S bond length of 1.92 Å is shorter than the bond length of 1.96 Å found in potassium dimethyldithiophosphate dihydrate,[3] or the average bond length of 1.95 Å found for the P=S double bond in the phosphorus sulphides,[14] but these differences are hardly significant.

The C_1—O_1—P—O_2—C_2 group is nearly planar, C_1 and C_2 being 0.35 and 0.08 Å away from the plane through O_1, P, and O_2. The interplanar angle O_1PO_2/S_2PS_1 is 90.5°. The P—O_1 and P—O_2 bonds are 1.57 and 1.59 Å, but the difference is not significant. The short P—O bond length implies a considerable amount of double bond character. This is probably due to overlap of *p*-orbitals of the oxygens with *d*-orbitals on phosphorus as proposed for phosphates by Cruickshank.[15]

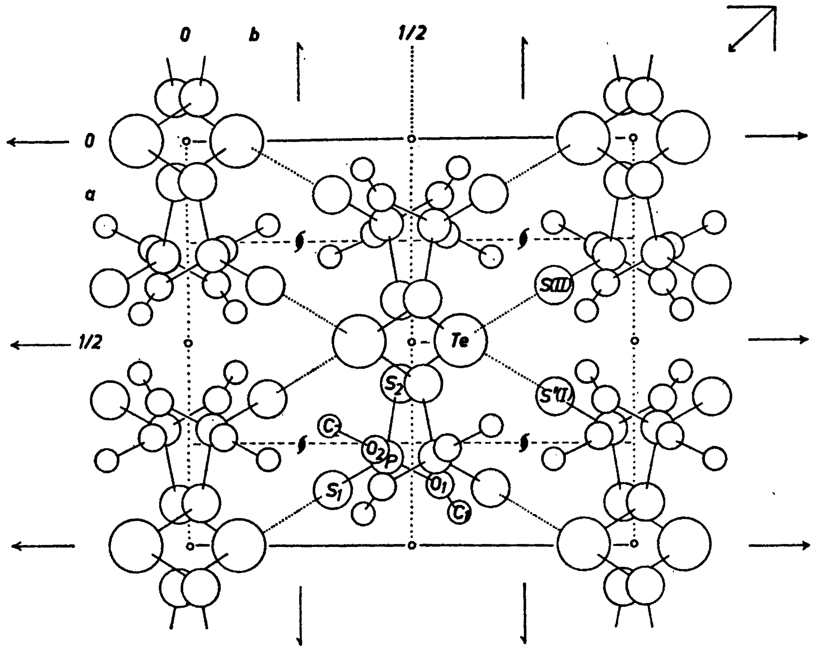

Fig. 2. The molecular arrangement of tellurium bis(dimethyldithiophosphate) seen along the *c*-axis.

The dihedral angle PS_2Te/S_2TeS_2' and the interplanar angle $S_2'TeS_2/S_2PS_1$ are 90.7 and 92.3°, respectively. The primed letters denote atoms in the other half of the molecule which are related to the first half (Table 2) by a twofold symmetry axis.

THE PACKING IN THE CRYSTALS

The molecular arrangement seen along the *c* axis is shown in Fig. 2. Two and two molecules are related through centres of symmetry, glide planes and twofold screw axes. The weak, intermolecular $Te\cdots S$ bonds indicated by dotted lines in Fig. 2, give rise to two-dimensional molecular layers parallel with (110).

The short, non-bonded intramolecular S—S distance in the dimethyldithiophosphate group in relation to the large covalent radius of tellurium of 1.37 Å [13] probably makes mono-nuclear complex formation difficult. Thus, instead of discrete mono-nuclear complex molecules with both sulphur atoms of a thiophosphate anion bonded to the same tellurium atom, the result is the polymeric network of Fig. 2. In the trivalent arsenic [16] and antimony [17] ethylxanthates, the same situation arises, but there both sulphur atoms of one anion form greatly asymmetric bonds to the same arsenic or antimony atom.

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Received September 18, 1965.