Acta Cryst. (1968). B**24**, 1262

The Crystal Structure of the 1:4 Thallous Dihydrogen Phosphate–Thiourea Complex

By L. H. W. Verhoef* and J. C. A. Boeyens†

Chemical Physics Group of the National Physical and Chemical Research Laboratories,
CSIR, Pretoria, South Africa

(*Received* 6 *November* 1967)

The crystal structure of the complex $TlH_2PO_4.4(SCN_2H_4)$ has been determined by three-dimensional X-ray diffraction methods. Columns of thallous ions were found to be enclosed by the thiourea sulphur atoms which lie at the corners of distorted Archimedean antiprisms centring at the positions of the thallous ions. This arrangement is similar to that found for the thiourea complexes of $TlClO_4$ and $TlNO_3$. The phosphate ions were found to occupy positions different from those of the perchlorate and nitrate ions. Whereas the latter anions occupy positions of optimum packing the phosphate ions are in positions more favourable for hydrogen bonding.

Introduction

The family of thiourea complexes of the alkali metal and thallous salts described by Boeyens & Herbstein (1966) can be subdivided into five classes. The structure types of three of these classes have been determined (Boeyens & Herbstein, 1967; Boeyens, 1968 *a, b*). A fourth, characterized by the space group *Cccm*, includes the complexes of Tl_2CO_3, $TlNO_2$ and TlH_2PO_3. As pointed out before (Boeyens & Herbstein, 1967) the crystals of the Tl_2CO_3 and $TlNO_2$ complexes are not suitable for crystallographic analyses because of their complicated domain structures. Although crystals of the present complex are also invariably twinned macroscopically, it was considered the most suitable for detailed examination. Another reason for selecting the phosphate comes from the work of Pfrepper (1966) who claims the preparation of a $Tl_3PO_4.6(TU)$ (TU = thiourea) complex. In our experience the existence of these complexes relates to the formation of coordination columns with a Tl:S ratio of 1:4, which is at variance with the Pfrepper formulation.

Sample preparation

Pfrepper (1966) obtained buff-coloured crystals by slow cooling of an aqueous solution containing Tl_3PO_4 and thiourea. Our attempt to repeat the preparation led to the precipitation of Tl_2S together with a white complex of microcrystalline quality. This is reminiscent of the reaction between $Pb(ClO_4)_2$ and thiourea which in aqueous solution leads to the precipitation of PbS and the formation of a 6:1 complex not of the present type (Boeyens & Herbstein, 1967) whilst in perchloric acid medium (Mahr & Ohle, 1939) no precipitation occurs and the 6:1 complex which is formed belongs to the present family. Acidification with orthophosphoric acid introduces the anion $H_2PO_4^-$ in excess. Thus, although the precipitation of Tl_2S is suppressed by addition of H_3PO_4, the complex of TlH_2PO_4 and not that of Tl_3PO_4 is obtained.

Slow cooling of the acidified solution of Tl_3PO_4 and thiourea in water yields twinned needles of $TlH_2PO_4.4(TU)$. Good single crystals were obtained by mechanically splitting these along their needle axes.

Crystallographic data

The cell constants were measured from an [001] oscillation photograph and *hk*0 and *hk*1 Weissenberg photographs.

$$a = 15{\cdot}40 \pm 0{\cdot}05,\ b = 14{\cdot}64 \pm 0{\cdot}05,\ c = 8{\cdot}27 \pm 0{\cdot}05\ \text{Å}.$$

The density of 2·153 g.cm^{-3} calculated for four formula units per unit cell compares well with the density of 2·151 g.cm^{-3} as measured by flotation. The conditions for possible reflexions: *hkl* for $h+k=2n$, $0kl$ for $l=2n$ and $h0l$ for $l=2n$, define the space group *Cccm* (No. 66 in *International Tables for X-ray Crystallography*, 1952) or its non-centrosymmetric counterpart which was ruled out by the successful structure analysis using *Cccm*.

Determination and refinement of the structure

Standard techniques and computer programs, described before (Boeyens, 1968*b*), were used to calculate a three-dimensional Patterson synthesis from 661 visually collected *hkl* data (including 54 unobserved). The coordinates derived for the Tl, S and P atoms were used to derive the phases for a Fourier synthesis from which all other atomic positions were obtained. Full-matrix least-squares refinement, using individual iso-

---

* Present address: Hydrological Research Section, Department of Water Affairs, Pretoria, South Africa.

† To whom all correspondence should be addressed.

tropic temperature factors without differential weighting, terminated with a residual, $R=\Sigma|F_o-F_c|/\Sigma F_o=0{\cdot}093$. The last cycle yielded parameter shifts of less than 0·1 of their e.s.d.'s. The final atomic parameters and their e.s.d.'s are given in Table 1, whilst the observed and calculated structure factors on an absolute scale ($F_{000}=1088$) are compared in Table 2. All unobserved reflexions have $F\leq 27$ in Table 2.

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

	x	*y*	*z*	*B*
Tl	0	0	$\frac{1}{4}$	3·85 Å^2
				0·06
S(1)	0·1039	0·1496	0	3·55
	0·0006	0·0006		0·21
S(2)	0·1470	0·1075	$\frac{1}{2}$	3·41
	0·0006	0·0006		0·20
C(1)	0·2115	0·1188	0	3·78
	0·0024	0·0025		0·75
C(2)	0·1100	0·2215	$\frac{1}{2}$	3·40
	0·0022	0·0023		0·69
N(1)	0·2541	0·1047	0·1353	5·09
	0·0016	0·0016	0·0035	0·53
N(2)	0·0940	0·2608	0·3614	4·80
	0·0015	0·0016	0·0034	0·52
P	$\frac{1}{2}$	0	$\frac{1}{4}$	2·85
				0·23
O	0·4395	0·0585	0·1518	9·63
	0·0018	0·0019	0·0042	0·82

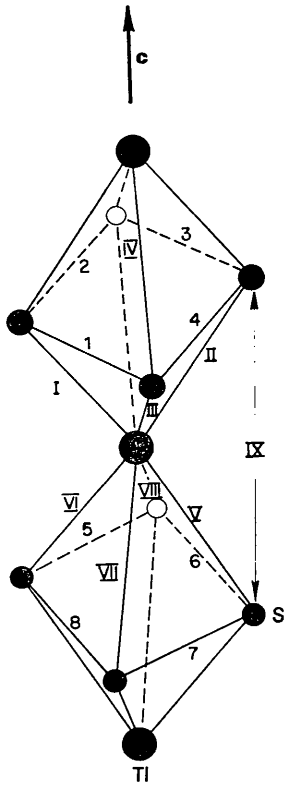

Fig. 1. Schematic representation of the arrangement of sulphur atoms around a chain of thallous ions. The interatomic distances are: 1 = 3 = 6 = 8 = 3·913 ± 0·014 Å, 2 = 4 = 5 = 7 = 3·822 ± 0·014 Å, I = II = VII = VIII = 3·446 ± 0·008 Å, III = IV = V = VI = 3·410 ± 0·008 Å, IX = 4·233 ± 0·014 Å. The bond angles are (1–2) = (3–4) = (5–8) = (6–7) = 89·0 ± 0·3°, (2–3) = (1–4) = (5–6) = (7–8) = 91·0 ± 0·3°.

Description of the structure

The structure can best be described in terms of coordination columns consisting of linear arrays of thallous ions which are 4·13 Å apart in the chain and each of which is surrounded by eight sulphur atoms at the corners of an Archimedean antiprism distorted towards a cube. Although these columns only have symmetry 2 they are remarkably similar to the tetragonal $(Tl^+{-}S_4)_n$ columns found in the complexes of $TlClO_4$ and $TlNO_3$ (Boeyens & Herbstein, 1967). The important dimensions of the coordination polyhedron are shown in Fig. 1. The angle of distortion of the antiprism is 26°.

The details of the packing are illustrated in Fig. 2, which shows the (001) projection of the structure. Although the thiourea molecules appear to be slightly distorted, they possess *mm* symmetry to within the limits of experimental error. The molecular dimensions of the thiourea molecule do not differ significantly from the dimensions of free thiourea (Truter, 1967) and need not be reproduced here. The environment of the phosphate is shown in more detail in (010) projection, in Fig. 3. The unsymmetrical anion, $H_2PO_4^-$, occupies a position of symmetry 222. Oxygen atoms and hydroxyl groups are thus statistically superimposed to mimic a tetrahedral arrangement. The P–O bond length is 1·5 ± 0·03 Å and the two OPO angles are 103 ± 2° and 114 ± 2°. There is thus considerable disorder which is also reflected in the high Debye–Waller factor observed for oxygen. The closest approach between the average position of such a disordered oxygen atom and a nitrogen atom associated with a thiourea molecule is 2·94 ± 0·04 Å. This is well within the range of O–H–N hydrogen bonds given by Pimentel & McClellan (1960).

Discussion of the structure

The most significant feature of this structure is the position occupied by the anion. In contradistinction to anions such as perchlorate, nitrate, bromide, iodide, sulphate (Boeyens & Herbstein, 1967), hydrated fluoride (Boeyens, 1968*a*) and chloride (Boeyens, 1968*b*), which all lie in the same mirror planes as the thiourea molecules when their salts form this type of complex, the phosphate occupies a position halfway between these mirror planes. As shown schematically in Fig. 4, this type of position (1) is much more favourable for hydrogen bonding with the amine groups than the in-plane type of position (2). Since the complexes of thallous dihydrogen phosphate, carbonate and nitrite constitute an isomorphous series (Boeyens & Herbstein, 1967) it is fairly certain that hydrogen bonds play a similar rôle in all these complexes. These anions differ from those mentioned above in that they all derive from relatively weak acids. There would thus seem to be an inverse parallel between pK_α values of acids and the tendency of their anions to form hydrogen bonds. Although this tendency does not seem to have been described before, the direct correlation between pK_α values and hydrogen bonding of carboxylic acids has been described in detail by Allen & Caldin (1953). It is suggested that these two phenomena are different aspects of the same effect. Highly ionizable hydrogen atoms (in strong acids) have a higher tendency than weaker acids to form hydrogen bonds, whereas the anions of weak acids are more firmly attached to their hydrogen atoms in the acid, so that after ionization they should have a higher affinity for hydrogen atoms and hydrogen bonding than the anions of the strong acids. It was considered interesting to see how far these ideas would be substantiated by the structures of the thiourea complexes of thallous formate and oxalate.

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

K	Fo	Fc
H=0, L=0		
2	314	324
4	159	157
6	143	131
8	332	313
10	207	159
12	143	125
14	76	78
16	57	51
18	52	63
H=1, L=0		
1	264	271
3	97	81
5	182	169
7	282	268
9	189	168
11	99	107
13	66	79
15	47	48
17	24	26
H=2, L=0		
0	306	352
2	287	319
4	418	445
6	279	284
8	174	160
10	115	96
12	170	139
14	114	118
16	57	65
18	26	38
H=3, L=0		
1	78	79
3	312	298
5	292	281
7	182	153
9	95	97
11	99	102
13	95	89
15	53	66
17	28	33
H=4, L=0		
0	178	166
2	367	427
4	248	266
6	219	231
8	144	152
10	192	191
12	123	110
14	92	80
16	73	78
18	20	39
H=5, L=0		
1	193	190
3	272	277
5	202	170
7	130	92
9	153	144
11	99	102
13	44	45
15	45	47
17	52	53
H=6, L=0		
0	96	97
2	310	318
4	200	224
6	208	226
8	150	159
10	191	191
12	93	92
14	63	59
16	52	64
H=7, L=0		
1	264	264
3	180	169
5	129	103
7	114	89
9	135	135
11	91	89
13	37	46
15	19	25
17	37	38
H=8. L=0		
0	304	294
2	188	185
4	136	138
6	158	172
3	172	187
10	145	136
12	98	92
14	60	64
16	25	37
H=9, L=0		
1	187	187
3	111	106
5	150	140
7	130	128
9	51	52
11	52	39
13	78	73
15	48	45
H=10, L=0		
0	198	181
2	105	96
4	213	207
6	205	193
8	147	128
10	38	36
12	93	88
14	76	89
16	20	37
H=11, L=0		
1	123	112
3	97	104
5	122	116
7	112	101
9	22	32
11	42	40
13	56	57
15	37	39
H=12, L=0		
0	177	161
2	140	130
4	142	126
6	114	98
8	132	105
10	83	80
12	63	68
14	31	40
H=13, L=0		
1	89	90
3	96	92
5	44	48
7	54	58
9	83	70
11	63	58
13	14	13
H=14, L=0		
0	95	92
2	154	129
4	120	88
6	68	64
8	81	76
10	81	88
12	28	39
H=15, L=0		
1	53	56
3	87	74
5	42	44
7	28	32
9	61	57
11	42	40
H=16, L=0		
0	62	51
2	108	88
4	86	82
6	56	65
8	38	40
10	39	50
H=17, L=0		
1	27	26
3	54	48
5	68	64
7	30	30
9	15	17
H=18, L=0		
0	56	56
2	40	47
4	46	55
6	51	59
H=19, L=0		
1	45	45
H=1, L=1		
3	105	-95
5	80	76
7	46	-41
9	24	-22
11	33	27
13	19	17
H=2, L=1		
2	20	20
4	108	110
6	11	19
8	90	-94
10	16	12
12	61	58
14	19	-15
16	23	-26
H=3, L=1		
1	82	69
3	42	-43
5	68	68
7	111	-118
9	25	-26
11	51	55
13	19	24
15	25	-27
H=4, L=1		
2	50	-41
4	50	44
6	59	52
8	8	0
10	16	-10
H=5, L=0		
1	92	-95
3	123	-142
5	7	-6
7	77	73
9	22	21
11	44	-45
13	11	-17
15	17	18
H=6, L=1		
2	10	-6
4	16	-19
6	26	22
8	61	64
10	30	-26
12	48	-39
14	10	11
16	20	19
H=7, L=1		
1	32	28
3	74	86
5	98	-97
7	15	3
9	29	17
11	11	-8
H=8, L=1		
2	112	113
4	8	-4
6	74	-66
8	10	4
10	18	20
H=9, L=1		
1	19	22
3	41	56
5	37	-40
7	10	-12
9	11	3
11	19	15
H=10, L=1		
2	9	-7
4	9	-2
6	10	7
8	26	-20
H=11, L=1		
1	32	-25
3	39	-35
5	60	50
7	11	10
9	19	-17
H=12, L=1		
2	69	-74
4	10	-5
6	44	43
8	19	-6
H=13, L=1		
1	26	-17
3	32	-33
5	46	36
H=14, L=1		
2	11	3
4	11	11
6	10	-10
8	10	-9
10	9	1
12	11	13
H=15, L=1		
1	26	21
3	32	27
H=16, L=1		
2	30	26
H=17, L=1		
1	9	8
3	9	9
5	25	-20
H=18, L=1		
2	14	3
H=0, L=2		
2	360	-365
4	443	-441
6	248	-223
8	145	-126
10	151	-148
12	141	-131
14	92	-90
16	71	-82
18	11	-32
H=1, L=2		
3	103	-314
5	242	-227
7	134	-135
9	111	-111
11	117	-117
13	71	-61
15	57	-62
17	32	-40
H=2, L=2		
0	353	-360
2	346	-334
4	275	-258
6	233	-202
8	220	-202
10	158	-170
12	118	-107
14	69	-72
16	67	-69
18	35	-48
H=3, L=2		
1	313	-311
3	138	-115
5	129	-113
7	198	-172
9	170	-169
11	93	-93
13	47	-56
15	31	-34
17	39	-38
H=4, L=2		
0	432	-447
2	263	-257
4	165	-162
6	246	-222
8	201	-213
10	150	-143
12	103	-109
14	79	-83
16	37	-39
18	28	-49
H=5, L=2		
1	235	-236
3	126	-114
5	194	-184
7	169	-160
9	97	-92
11	68	-59
13	89	-95
15	35	-41
17	12	-18
H=6, L=2		
0	242	-235
2	227	-203
4	234	-228
6	257	-252
8	142	-150
10	83	-83
12	120	-106
14	114	-104
16	35	-45
H=7, L=2		
1	149	-146
3	173	-166
5	186	-173
7	126	-124
9	63	-61
11	61	-56
13	75	-71
15	56	-53
17	13	-23
H=8, L=2		
0	147	-140
2	216	-208
4	221	-209
6	202	-162
8	131	-127
10	118	-116
12	84	-86
14	58	-61
16	48	-55
H=9, L=2		
1	111	-120
3	176	-175
5	92	-92
7	70	-68
9	101	-92
11	83	-87
13	18	-23
15	27	-30
H=10, L=2		
0	141	-145
2	193	-184
4	159	-151
6	96	-89
8	121	-119
10	135	-134
12	64	-67
14	14	-25
H=11, L=2		
1	118	-119
3	121	-109
5	65	-58
7	61	-63
9	88	-90
11	71	-65
H=12, L=2		
0	144	-141
2	125	-121
4	119	-117
6	109	-101
8	92	-95
10	77	-74
12	53	-54
14	30	-44
H=13, L=2		
1	76	-69
3	60	-67
5	104	-96
7	67	-67
9	26	-30
11	27	-24
13	38	-47
H=14, L=2		
0	109	-98
2	89	-78
4	103	-102
6	114	-109
8	60	-59
10	22	-27
12	39	-52
H=15, L=2		
1	67	-64
3	27	-38
5	64	-60
7	60	-56
9	15	-26
H=16, L=2		
0	113	-99
2	78	-73
4	39	-43
6	62	-60
8	58	-61
10	28	-44
H=17, L=2		
1	56	-55
3	37	-33
5	14	-17
7	27	-34
H=18, L=2		
0	34	-46
2	57	-59
4	43	46
6	22	34
H=19, L=2		
1	9	16
3	34	42
H=1, L=3		
1	17	11
3	107	98
5	29	34
7	51	-51
9	50	-50
11	50	49
13	10	18
15	9	-16
17	16	-15
H=2, L=3		
2	22	-24
4	9	7
6	7	7
8	99	-102
10	38	35
12	41	43
14	10	0
16	27	-29
H=3, L=3		
1	85	-66
3	40	42
5	53	57
7	22	16
9	45	-43
11	40	36
H=4, L=3		
2	67	-73
4	42	-41
6	21	16
8	25	-23
10	16	13
H=5, L=3		
1	10	-16
3	25	17
5	28	22
7	40	45
9	9	0
11	35	-28
13	17	-12
H=6, L=3		
2	49	-46
4	53	-51
6	8	-6
8	65	62
10	24	-24
12	18	-27
14	9	8
16	11	20
H=7, L=3		
1	49	47
3	7	-0
5	24	-24
7	9	14
9	34	38
11	40	-34
H=8, L=3		
2	78	93
4	8	8
6	66	-76
8	24	12
10	18	7
H=9, L=3		
1	72	73
3	50	42
5	22	-19
7	58	-54
H=10, L=3		
2	9	-6
4	9	10
6	24	14
H=11, L=3		
1	50	-49
3	51	-59
5	34	31
7	18	24
9	17	-12
H=12, L=3		
2	50	-47
4	10	5
6	44	45
H=13, L=3		
1	25	-27
3	10	-4
5	10	8
7	10	0
9	9	-14
13	13	13
H=16, L=3		
2	26	27
4	8	1
6	19	-20
H=17, L=3		
1	23	16
3	13	10
5	16	-14
H=0, L=4		
2	212	-217
4	114	102
6	261	243
8	201	189
10	139	129
12	69	82
14	63	79
16	31	36
H=1, L=4		
1	292	272
3	106	93
5	133	120
7	118	127
9	116	114
11	58	54
13	76	70
15	16	29
17	20	27
H=2, L=4		
0	209	221
2	227	222
4	194	179
6	220	199
8	151	151
10	112	125
12	90	99
14	70	77
16	32	43
H=3, L=4		
1	107	101
3	237	216
5	186	184
7	93	99
9	43	52
11	77	73
13	66	64
15	54	53
H=4, L=4		
0	84	93
2	194	193
4	308	299
6	189	166
8	129	115
10	83	97
12	86	93
14	60	68
16	53	67
H=5, L=4		
1	116	112
3	184	189
5	79	99
7	91	93
9	86	95
11	92	94
13	11	19
15	41	42
H=6, L=4		
0	254	253
2	212	200
4	166	164
6	88	75
8	146	149
10	132	140
12	68	78
14	23	28
16	37	50
H=7, L=4		
1	124	131
3	104	110
5	74	80
7	82	92
9	99	99
11	77	75
13	24	29
15	18	23
H=8, L=4		
0	207	196
2	147	150
4	134	140
6	139	136
8	102	110
10	70	76
12	64	69
14	46	59
H=9, L=4		
1	116	114
3	44	56
5	100	106
7	99	98
9	61	58
11	26	28
13	52	58
15	12	28
H=10, L=4		
0	166	150
2	127	127
4	82	98
6	125	142
8	73	82
10	45	48
12	50	58
14	49	66
H=11, L=4		
1	72	68
3	68	69
5	108	102
7	79	70
9	26	31
11	9	24
13	40	51
H=12, L=4		
0	75	79
2	106	110
4	92	97
6	90	97
8	53	61
10	45	57
12	37	48
H=13, L=4		
1	70	74
3	77	65
5	33	30
7	44	40
9	49	57
11	30	44
H=14, L=4		
0	83	88
2	87	92
4	55	60
6	17	36
8	65	68
10	62	72
H=15, L=4		
1	35	40
3	67	61
5	28	33
7	8	27
9	27	35
H=16, L=4		
0	22	37
2	47	50
4	77	80
6	40	48
8	21	35
H=17, L=4		
1	23	23
3	28	37
5	31	43
H=18, L=4		
0	42	51
2	20	34
H=1, L=5		
3	33	26
5	27	23
7	40	-37
9	31	-29
11	33	33
H=2, L=5		
4	28	34
6	7	10
8	62	-67
10	23	18
12	33	33
14	8	-4
16	16	-21
H=3, L=5		
1	28	-26
3	6	-4
5	32	30
7	20	-18
9	27	-25
11	33	31
H=4, L=5		
2	32	-32
4	7	1
6	27	26
H=5, L=5		
1	26	-26
3	24	-27
5	8	1
7	35	32
9	9	5
11	28	-22
H=6, L=5		
2	21	-15
4	27	-22
6	8	6
8	47	45
10	17	-18
12	26	-24
H=7, L=5		
1	31	26
3	14	12
5	34	-35
7	9	8
9	17	23
11	16	-19
H=8, L=5		
2	62	68
4	9	4
6	49	-50
H=9, L=5		
1	44	41
3	36	35
5	9	-17
7	29	-30
9	9	5
11	14	12
H=11, L=5		
1	33	-29
3	33	-35
5	33	29
H=12, L=5		
2	37	-41
4	9	-0
6	27	31
H=16, L=5		
2	16	20

These complexes were therefore prepared by dissolving the constituents in the ratios COOTl:4(TU) and $(OOC)_2Tl_2$:8(TU) in boiling water. In both cases needles crystallized on cooling. The crystals of the formate complex were however too small for single-crystal investigations and other techniques are now being used to obtain suitable crystals. Crystals of the oxalate complex are not isomorphous but could be related to the *Cccm* group. For the oxalate complex

$a=15{\cdot}91$, $b=13{\cdot}24$, $c=8{\cdot}39$ Å
$\varrho_{\rm calc}=2{\cdot}078$ g.cm^{-3}, $Z=2$, $\varrho_{\rm obs}=2{\cdot}21$ g.cm^{-3}
Space group: *Pnnm* .

These results suggest that a structural method could be developed which would allow differentiation between strong and weak hydrogen-bonding anions.

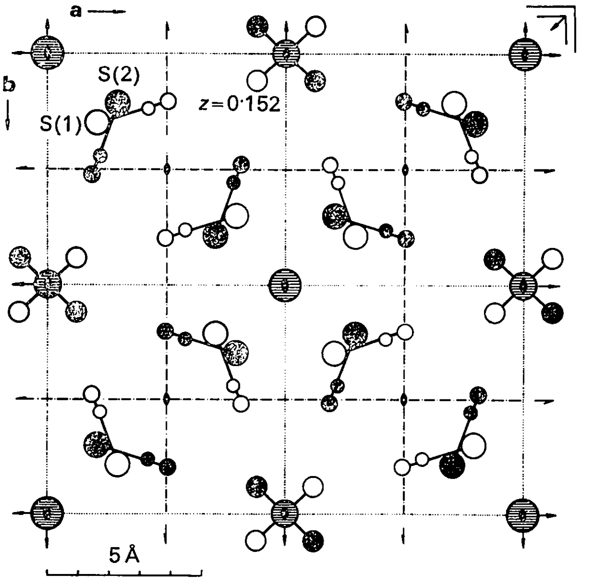

Fig. 2. Projection of the structure along [001]. Shaded circles represent atoms lying at $c=\frac{1}{4}$. Open and full circles refer to atoms lying above and below this plane respectively. All the symmetry axes parallel to the paper are at $c=\frac{1}{4}$.

The thallous orthophosphate complex

If, as assumed before (Boeyens, 1968*b*), complexes of monovalent cations which belong to the present family are formed only if the cation:thiourea ratio is 1:4 (the ratio required to form the familiar coordination columns as described in this paper) the complex of Tl_3PO_4 should present a very interesting special case. In the structure of Tl_3PO_4.12(TU), assuming it to belong to this family, the anionic channel must be severely underpopulated. Unless structural water stabilizes the structure, collapse seems inevitable. The complex formulated as Tl_3PO_4.6(TU) by Pfrepper (1966) was therefore examined crystallographically, firstly to establish whether it is a single phase and secondly to analyse the structure. Up to the time of writing we have had no success in obtaining suitable crystals for single-crystal work. From the powder pattern however, we infer that it is a single phase, and is in many respects similar to the present series of complexes. As shown in Table 3, the powder pattern of the complex can be indexed in terms of a hexagonal unit cell with $a=22{\cdot}88$, $c=7{\cdot}91$ Å. For $Z=4$ the density is calculated as 2·16 g.cm^{-3}. No attempt was made to determine the density of the powder experimentally, but compared with the 2·15 g.cm^{-3} for TlH_2PO_4.4(TU) it appears to be

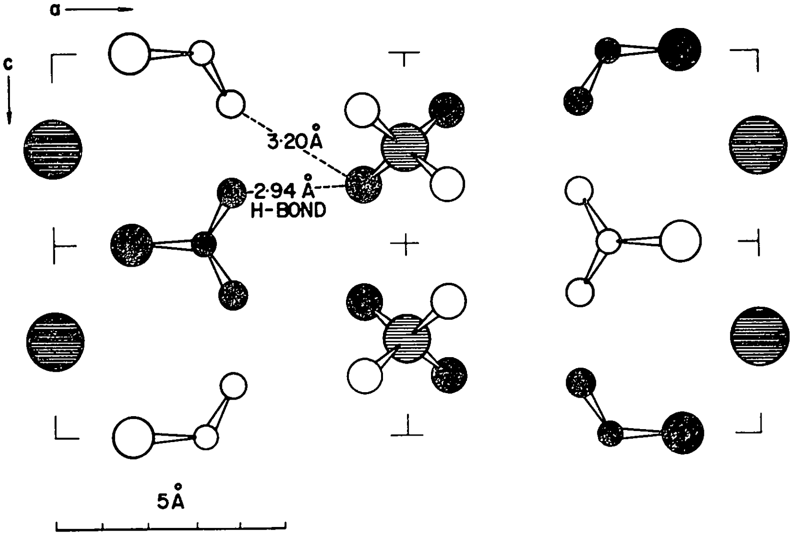

Fig. 3. (010) projection of the surroundings of the phosphate ion. Only molecules in non-overlap positions are shown to illustrate the system of hydrogen bonds.

Table 3. *Powder diffractometer pattern of* Tl_3PO_4–6TU, *indexed for a hexagonal unit cell with* $a=22·88$, $c=7·91$ Å

The intensities are non-integrated and estimated from peak heights. The *d* values were obtained from NBS *Tables for Conversion of X-ray Diffraction Angles to Interplanar Spacing* (1950).

d	Intensity	$\sin^2\theta$ (obs)	$\sin^2\theta$ (calc)	Index
11·472 Å	10	0·0045	0·0045	110
9·883	38	0·0061	0·0061	200
7·4806	41	0·0106	0·0106	210
6·1712	2	0·0156	0·0156	201
5·7339	100	0·0181	0·0182	220
4·9511	11	0·0242	0·0242	400
4·5207	13	0·0291	0·0288	320
3·9551	1	0·0379	0·0379	500
3·8209	3	0·0406	0·0409	330
3·7261	6	0·0427	0·0424	420
3·6715	6	0·0440	0·0441	202
3·5643	22	0·0467	0·0470	510
3·2063	10	0·0577	0·0577	312
3·1530	26	0·0596	0·0591	520
3·0193	6	0·0651	0·0651	610
2·9134	7	0·0699	0·0698	412
2·8642	21	0·0723	0·0727	440
2·7944	7	0·0760	0·0759	502
2·7509	26	0·0784	0·0788	620

of the correct magnitude. For comparison, the cell constants of the complex KI.4(TU), $Z=8$, space group $P4/mnc$, are $a=20·29$, $c=8·29$ Å (Boeyens & Herbstein, 1967).

Conclusion

It has been shown that in the TlH_2PO_4.4(TU) complex, the arrangement of thallous ions corresponds to that found previously for $TlClO_4$ and $TlNO_3$, but that the $H_2PO_4^-$ occupies a position structurally different from that occupied by ClO_4^- and NO_3^-. This difference is ascribed to different hydrogen-bonding characteristics and infrared work to substantiate this assumption is now in progress. Also in progress are further attempts to grow single crystals of the complex Tl_3PO_4.6(TU) which represents the first known example of an ionic thiourea complex where the effect of the anion is sufficient to disrupt the cationic arrangement completely.

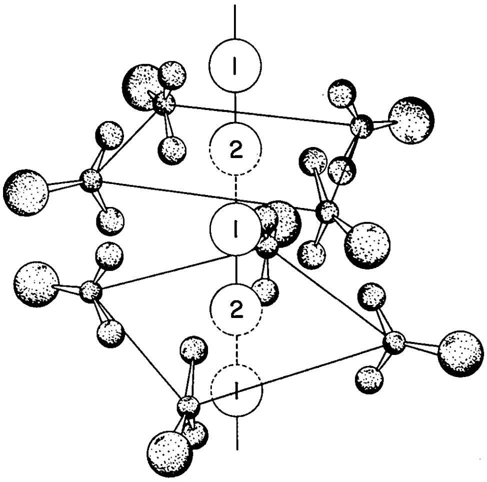

Fig. 4. Perspective view of a set of thiourea molecules surrounding the anionic channel. Position 1 halfway between the mirror planes is more favourable for hydrogen bonding than position 2, in the mirror plane.

References

Allen, G. & Caldin, E. F. (1953). *Quart. Rev. Chem. Soc. Lond.* 7, 255.
Boeyens, J. C. A. (1968*a*). *Acta Cryst.* **B24,** 199.
Boeyens, J. C. A. (1968*b*). *Acta Cryst.* **B24,** 1191.
Boeyens, J. C. A. & Herbstein, F. H. (1966). *Nature, Lond.* **211**, 588.
Boeyens, J. C. A. & Herbstein, F. H. (1967). *Inorg. Chem.* **6**, 1408.
International Tables for X-ray Crystallography (1952). Vol. I, p. 155. Birmingham: Kynoch Press.
Mahr, C. & Ohle, H. (1939). *Liebigs Ann.* **542**, 44.
Pfrepper, G. (1966). *Z. anorg. allg. Chem.* **347**, 160.
Pimentel, G. C. & McClellan, A. L. (1960). *The Hydrogen Bond*, p. 289 San Francisco: W. H. Freeman & Co.
Tables for Conversion of X-ray Diffraction Angles to Interplanar Spacing (1950). NBS Applied Mathematics Series 10. Washington: U.S. Government Printing Office.
Truter, M. R. (1967). *Acta Cryst.* **22**, 556.