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

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The crystal structure of the complex $C_6H_5COOTl.4(SCN_2H_4)$ has been determined by three-dimensional X-ray diffraction methods. This structure is characterized by $(Tl^+.4TU)_n$ coordination columns (TU = thiourea) with *mm* symmetry and is similar to those with $4/m$ symmetry observed before in the TU complexes of other thallous salts. The benzoate ions also occur in linear stacks and the amino ends of the thiourea molecules which surround such a stack do not all interact with the anions in an equivalent fashion. Those facing the carboxyl group directly are strongly hydrogen-bonded to it and the dipole moment of the thiourea molecule is enhanced because of this. This enhancement leads to stronger interaction of the sulphur, not only with the thallous ion, but also with a similarly activated neighbouring sulphur atom. This latter interaction probably involves weak π-bonding and it leads to a distortion of the coordination column away from the familiar fourfold symmetry.

Introduction

The idea (Boeyens, 1968*b*) that the structure of an ionic thiourea complex is completely determined by the close packing of tetragonal $(M^+.4TU)_n$ coordination columns is not strictly correct. The very existence of such a column is for instance refuted by the stoichiometry of the complex $Tl_3PO_4.6TU$, the structure of which has not been determined but which appears to be a typical ionic complex (Verhoef & Boeyens, 1968). Complete disruption of the expected column is caused here by the relatively small number of anions available. Excessively large voids would exist had the normal type of packing prevailed. Another instance where the geometry of the column is affected by the anion is found in the structure of $TlClO_4.4TU$ (Boeyens & Herbstein, 1967). In this case two types of column are found in the same structure. One of these is slightly distorted to allow for anionic protrusion.

Since these structures usually involve heavy cations, the interatomic distances are not generally sufficiently accurate to detect small distortions in the coordination columns, particularly when these distortions have the same symmetry as the column. It is thus desirable to investigate the effect of an anion which is large enough possibly to perturb the column, but not symmetrical enough to have the same effect on all sides of the column. A likely candidate appeared to be the benzoate ion whose thallous salt forms a well defined complex with thiourea.

Crystal data

The complex was crystallized by cooling an aqueous solution containing thallous benzoate and thiourea in stoichiometric proportions. The cell dimensions and space group (orthorhombic) of a needle-shaped crystal of the complex with an average diameter of 0·01 cm, were determined from appropriate oscillation and Weissenberg photographs: $a = 15{\cdot}64 \pm 0{\cdot}05$ Å, $b = 17{\cdot}09 \pm 0{\cdot}5$ Å, $c = 8{\cdot}15 \pm 0{\cdot}05$ Å. The density as measured by flotation is 1·95 cm^{-3} and the density calculated for 4 formula units per unit cell is 1·92 cm^{-3}. The conditions for possible reflexions: *hkl* for $h+k=2n$ and *h*0*l* for $l=2n$ are consistent with the space groups $Cmc2_1$ and *Cmcm*. The latter centrosymmetric space group (No. 63 in*for X-ray Crystallography International Tables*, 1952) was successfully used for the structure determination.

Determination and refinement of the Structure

The space group for this complex differs from all others encountered previously for this family of thiourea complexes in that it has no mirror planes at $z=0,\frac{1}{2}$, but instead has mirror planes at $z=\frac{1}{4},\frac{3}{4}$. For the complex to have a related type of structure this requires the Tl^+ ion to occupy either positions *a* or *b*, symmetry $2/m$, of the space group. This observation led to the correct interpretation of the three-dimensional Patterson synthesis based on 980 *hkl*, visually estimated, data which were collected and corrected by standard techniques described earlier (Boeyens, 1968*b*) with Cu $K\alpha$ (Ni filtered) radiation. Full-matrix least-squares refinement using individual isotropic temperature factors without differential weighting terminated with a residual, $R = \Sigma\,|F_o - F_c|/\Sigma\,F_o = 0{\cdot}091$. The parameter shifts in the last cycle were less than 0·1 of their estimated standard deviations. The final atomic parameters and their e.s.d.'s are given in Table 1, while the observed and calculated structure factors on an absolute scale ($F_{000} = 1128$) are given in Table 2. All unobserved reflexions have $F_{\rm obs} < 20$ in Table 2. The same computer

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program and atomic scattering factors described before (Boeyens, 1968*b*) were used in the analysis.

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

	x	*y*	*z*	*B* (Å^2)
Tl	0	0	0	3·09
				0·04
S(1)	0·1073	0·1236	$\frac{1}{4}$	2·55
	0·0004	0·0003		0·12
S(2)	0·1452	0·0942	$\frac{3}{4}$	3·00
	0·0004	0·0004		0·13
N(1)	0·2591	0·0944	0·1060	3·78
	0·0009	0·0008	0·0022	0·31
N(2)	0·1065	0·2332	0·6106	4·69
	0·0011	0·0009	0·0025	0·37
C(1)	0·2174	0·1025	$\frac{1}{4}$	3·07
	0·0016	0·0014		0·47
C(2)	0·1184	0·1946	$\frac{3}{4}$	2·91
	0·0015	0·0013		0·45
C(3)	0	0·3159	$\frac{1}{4}$	3·98
		0·0023		0·81
C(4)	0	0·4818	$\frac{1}{4}$	1·95
		0·0016		0·53
C(5)	$\frac{1}{2}$	0·0715	$\frac{1}{4}$	2·08
		0·0017		0·53
C(6)	0·0775	0·3584	$\frac{1}{4}$	4·14
	0·0019	0·0016		0·59
C(7)	0·0786	0·4416	$\frac{1}{4}$	3·48
	0·0016	0·0014		0·47
O	0·4294	0·1056	$\frac{1}{4}$	3·42
	0·0011	0·0010		0·34

Description of the structure

The structure is stabilized by ion-dipole attractions. The thallous ions, each of which is surrounded by eight sulphur atoms, arrange themselves in infinite linear chains. The benzoate ions with *mm* crystallographic symmetry are likewise stacked along [001] with their long axes alternately in the [010] and [0$\bar{1}$0] directions. All the atoms of the benzoate ions lie in the same mirror planes, at $z=\frac{1}{4},\frac{3}{4}$, which contain the sulphur and carbon atoms of the thiourea molecules. Each benzoate ion has a polar and an apolar end, the former referring to the carboxyl group. Only the polar ends seem to interact with neighbouring thiourea molecules in the same mirror plane. This is shown distinctly in the (001) projection of the structure depicted in Fig. 1. It is seen that the polar end is surrounded by four $=C(NH_2)_2$ groups mirrored in the plane of the benzoate, whereas the apolar end is surrounded at van der Waals distances by four sulphur atoms which are coordinated to thallous ions.

It is significant that the thiourea molecules do not interact identically with their neighbouring cations nor among themselves. Whereas one type is 3·45 Å distant from the closest thallous ion, another type approaches a thallous ion at a distance of 3·38 Å. Since $\sigma(\mathrm{Tl}\cdots\mathrm{S}) \sim 0{\cdot}006$ Å, this difference is chemically significant. Compared with $d(\mathrm{Tl}\cdots\mathrm{S})$ as observed in the structures of $TlNO_3.4TU$, $TlClO_4.4TU$ (Boeyens & Herbstein, 1967) and $TlH_2PO_4.4TU$ (Verhoef & Boeyens, 1968) the 3·45 Å distance is seen to be the normal one. Furthermore, the sulphur atoms of the thiourea molecules involved in these close approaches are abnormally close, at 3·36 ± 0·01 Å, compared with the 4·54 ± 0·01 Å between the sulphurs in van der Waals contact. There is an intermediate approach of 3·77 ± 0·01 Å between sulphur atoms belonging to thiourea molecules of unlike type. The average distance between sulphurs in the three structures mentioned above is halfway between the intermediate and the long approaches observed here. Sulphur atoms with $\Delta z=\frac{1}{2}$ and in positions of near-overlap in (001) projection are 4·15 ± 0·01 Å apart. The Tl–Tl distance in a stack ($c/2=4{\cdot}075$ Å) is somewhat smaller than the interthallous distance of 4·145 Å found in all other structures previously examined.

Bond lengths and interatomic distances

The important interatomic distances are shown in Fig. 1. Where no values are specified, regular van der Waals separations were observed.

There are two different types of thiourea molecule in the structure. The one type is involved in the close approaches described under the previous heading, whereas the other type is not. The bond lengths of the two types will now be examined for possible effects of the close approaches. The molecular parameters for the two types are compared in Table 3 with uncoordinated thiourea (Truter, 1967). Except for the long S–C bonds which are just not at significance level, the two types of molecule are very similar to free thiourea, and on this evidence are unaffected by any special interactions.

The benzoate ion has *mm* crystallographic symmetry. There are thus three crystallographically independent bonds in the benzene ring. These measure 1·41, 1·42

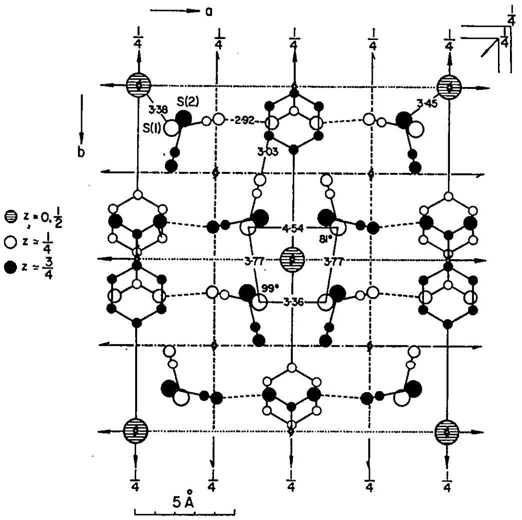

Fig. 1. Projection of the structure along [001] to show the details of the packing and some important structural parameters. Dashed lines indicate hydrogen bonds.

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

H	F_o	F_c
K=0, L=0		
4	106	108
6	87	86
8	365	356
10	231	205
12	181	167
14	116	119
16	103	88
18	84	80
K=1, L=0		
3	108	96
5	209	198
7	336	325
9	257	218
11	129	112
13	71	78
15	67	77
17	51	53
19	88	79
K=2, L=0		
2	245	239
4	317	182
6	284	268
8	215	188
10	137	121
12	181	169
14	149	146
16	86	83
18	48	51
K=3, L=0		
1	216	205
3	332	368
5	313	323
7	185	169
9	117	111
11	150	146
13	168	154
15	110	109
17	58	63
19	20	33
K=4, L=0		
0	42	28
2	319	347
4	286	286
6	315	305
8	195	168
10	197	193
12	128	118
14	112	95
16	90	92
18	42	62
K=5, L=0		
1	263	249
3	335	330
5	226	201
7	108	102
9	159	157
11	157	156
13	124	112
15	93	89
17	89	94
K=6, L=0		
0	44	20
2	331	329
4	287	274
6	279	257
8	144	128
10	193	193
12	101	110
14	77	79
16	73	85
18	67	68
K=7, L=0		
1	240	216
3	295	269
5	236	216
7	156	146
9	187	180
11	158	152
13	87	91
15	54	63
17	82	79
K=8, L=0		
0	336	323
2	258	220
4	157	128
6	135	115
8	172	178
10	165	170
12	95	99
14	44	56
16	48	57
18	65	70
K=9, L=0		
1	309	293
3	139	121
5	130	115
7	201	193
9	181	189
11	118	120
13	69	77
15	55	61
17	42	49
K=10, L=0		
0	319	302
2	134	123
4	193	179
6	172	167
8	176	184
10	68	69
12	96	94
14	91	99
16	53	62
K=11, L=0		
1	181	154
3	142	129
5	184	174
7	163	165
9	57	62
11	57	64
13	104	110
15	87	90
K=12, L=0		
0	172	158
2	125	119
4	194	186
6	185	171
8	121	122
10	37	48
12	91	98
14	95	100
16	52	54
K=13, L=0		
1	143	126
3	157	145
5	132	138
7	107	112
9	62	66
11	64	77
13	75	82
15	61	64
K=14, L=0		
0	86	83
2	159	145
4	129	124
6	103	114
8	72	84
10	90	97
12	68	74
14	44	51
K=15, L=0		
1	94	102
3	127	127
5	82	88
7	61	70
9	84	95
11	69	78
13	25	35
K=16, L=0		
0	80	95
2	128	139
4	80	73
6	55	65
8	66	79
10	112	119
12	45	49
K=17, L=0		
1	87	98
3	79	90
5	43	60
7	40	55
9	90	97
11	63	71
K=18, L=0		
0	75	77
2	75	81
4	65	76
6	38	55
8	34	48
10	54	60
K=19, L=0		
1	49	56
3	60	75
5	90	97
7	61	71
9	34	44
K=20, L=0		
0	67	68
2	27	41
4	47	65
6	49	57
K=21, L=0		
1	54	58
3	21	44
5	39	61
K=1, L=1		
3	62	-68
5	19	-20
7	43	52
9	37	-29
11	41	-42
13	28	20
15	26	19
17	10	-6
19	21	-12
K=2, L=1		
0	56	-51
2	55	47
4	85	-95
6	117	129
8	17	-12
10	68	-65
12	10	5
14	63	58
16	11	-7
18	37	-37
K=3, L=1		
1	47	-40
3	9	9
5	100	105
7	67	71
9	88	-94
11	48	-54
13	68	71
15	37	36
17	10	-21
19	24	-17
K=4, L=1		
0	84	-75
2	5	-3
4	70	-69
6	57	60
8	25	-26
10	38	-41
12	11	1
14	26	23
16	11	-19
18	16	-20
K=5, L=1		
1	96	92
3	54	-48
5	64	-62
7	24	19
9	60	57
11	19	11
13	25	-19
15	11	-18
17	10	8
19	18	17
K=6, L=1		
0	169	183
2	38	30
4	52	-52
6	97	-101
8	42	43
10	63	70
12	11	-9
14	40	-39
16	10	7
18	31	30
K=7, L=1		
1	73	-64
3	7	-2
5	14	-13
7	30	-30
9	59	53
11	24	17
13	63	-62
15	32	-29
K=8, L=1		
0	31	16
2	16	6
4	117	116
6	71	-75
8	30	-31
10	27	30
12	30	26
14	11	-6
16	18	15
K=9, L=1		
1	99	-92
3	63	54
5	55	47
7	34	-39
9	23	-21
K=10, L=1		
0	57	-60
2	8	-5
4	70	70
6	25	23
8	10	-13
10	11	-12
12	21	14
14	19	14
K=11, L=1		
1	9	-9
3	9	-2
5	10	-8
7	11	-17
9	55	-53
11	21	-19
13	28	22
15	20	16
K=12, L=1		
0	25	-24
2	10	6
4	10	-13
6	89	85
8	46	37
K=13, L=1		
1	69	60
3	53	-53
5	59	-61
7	11	6
9	12	-6
11	20	-11
K=14, L=1		
0	60	56
2	20	14
4	63	-68
6	26	15
8	40	32
K=15, L=1		
1	33	26
3	26	-28
5	21	-18
7	21	15
9	20	20
K=16, L=1		
0	21	20
2	12	1
4	12	1
6	21	-13
K=17, L=1		
1	33	-31
3	21	13
5	28	23
K=18, L=1		
0	20	-28
2	11	-5
4	42	48
K=19, L=1		
1	25	-30
3	28	29
5	20	21
7	23	-20
K=20, L=1		
0	27	-23
2	8	-2
4	23	20
K=0, L=2		
2	145	171
4	315	413
6	248	254
8	159	138
10	135	127
12	145	120
14	74	66
16	86	85
18	33	47
K=1, L=2		
1	258	283
3	301	437
5	260	270
7	154	140
9	148	135
11	215	200
13	175	143
15	140	118
17	83	82
19	20	37
K=2, L=2		
0	219	201
2	235	246
4	256	262
6	215	209
8	208	190
10	172	161
12	124	113
14	81	77
16	90	85
18	59	63
K=3, L=2		
1	320	323
3	195	187
5	199	190
7	256	237
9	246	228
11	156	136
13	88	89
15	73	74
17	91	78
19	69	68
K=4, L=2		
0	405	488
2	287	274
4	91	91
6	159	152
8	199	198
10	188	166
12	120	113
14	108	101
16	62	58
18	78	67
K=5, L=2		
1	310	299
3	148	138
5	234	224
7	268	257
9	215	205
11	116	105
13	113	114
15	66	68
17	54	51
19	57	79
K=6, L=2		
0	333	309
2	253	212
4	187	160
6	220	214
8	162	158
10	113	102
12	124	112
14	137	128
16	55	55
18	43	43
K=7, L=2		
1	236	204
3	216	181
5	238	220
7	198	191
9	110	110
11	89	85
13	129	123
15	100	95
17	38	46
K=8, L=2		
0	176	151
2	227	199
4	245	229
6	221	211
8	149	142
10	97	101
12	113	110
14	118	103
16	78	75
18	17	35
K=9, L=2		
1	156	132
3	254	235
5	197	189
7	126	124
9	89	88
11	114	113
13	94	87
15	91	81
17	55	59
K=10, L=2		
0	107	91
2	207	179
4	218	207
6	122	113
8	101	100
10	126	128
12	109	106
14	47	48
16	66	62
K=11, L=2		
1	159	147
3	226	202
5	144	134
7	107	107
9	135	135
11	129	129
13	40	47
15	39	48
K=12, L=2		
0	178	173
2	173	155
4	118	106
6	64	65
8	115	119
10	141	135
12	69	69
14	12	24
16	41	51
K=13, L=2		
1	174	162
3	109	107
5	92	86
7	106	108
9	128	134
11	91	88
13	38	44
15	29	40
K=14, L=2		
0	167	145
2	111	108
4	91	97
6	113	106
8	93	93
10	69	68
12	55	56
14	55	61
K=15, L=2		
1	115	104
3	86	90
5	129	127
7	96	102
9	50	58
11	43	47
13	82	84
K=16, L=2		
0	88	82
2	69	74
4	86	95
6	128	117
8	56	60
10	12	22
12	45	54
K=17, L=2		
1	95	87
3	65	72
5	90	90
7	89	84
9	39	41
11	30	36
K=18, L=2		
0	75	78
2	74	75
4	54	64
6	72	80
8	71	71
10	40	48
K=19, L=2		
1	69	74
3	59	61
5	20	34
7	35	44
K=20, L=2		
0	38	57
2	61	69
4	61	58
6	36	43
K=21, L=2		
1	37	50
3	48	56
K=1, L=3		
1	78	60
3	9	-3
5	46	-50
7	49	-53
9	77	81
11	33	36
13	26	-26
15	36	-35
17	17	17
K=2, L=3		
0	56	-34
2	76	69
4	29	-28
6	42	-50
8	25	-28
10	98	97
12	32	-28
14	37	-41
16	11	-3
18	45	40
K=3, L=3		
1	44	-39
3	23	18
5	15	5
7	80	-82
9	60	62
11	20	17
13	30	-30
15	39	-35
17	24	24
K=4, L=3		
0	59	-50
2	64	56
4	33	28
6	14	7
8	16	-23
10	50	46
12	11	-13
14	12	-4
16	10	11
18	21	18
K=6, L=3		
0	51	-63
2	41	-46
4	43	38
6	45	43
8	10	-5
10	53	-59
12	26	13
14	26	21
16	10	-3
18	21	-25
K=7, L=3		
1	16	7
3	37	29
5	42	36
7	46	40
9	72	-83
11	12	-9
13	53	53
15	42	42
17	24	-26
K=8, L=3		
0	15	11
2	67	-72
4	9	-10
6	45	37
8	42	43
10	55	-67
K=9, L=3		
1	102	97
3	45	-51
5	61	-72
7	51	46
9	25	22
K=10, L=3		
0	109	103
2	9	-3
4	69	-77
6	38	-48
8	40	34
10	26	19
12	11	-12
14	22	-26
K=11, L=3		
1	10	-2
3	10	6
5	20	20
7	11	10
9	48	42
11	21	11
13	10	-12
15	14	-14
K=12, L=3		
0	36	-39
2	31	15
4	32	12
6	39	-39
8	48	-60
10	12	14
K=13, L=3		
1	40	-46
3	51	40
5	59	56
7	12	-15
9	21	18
K=14, L=3		
0	40	-51
2	21	15
4	26	21
6	12	-5
8	25	-34
K=15, L=3		
1	12	-23
3	27	23
5	21	19
K=16, L=3		
0	26	-30
2	12	-7
4	21	14
6	28	17
K=17, L=3		
1	28	25
K=18, L=3		
0	50	50
2	10	-7
4	34	-39
6	9	-8
8	30	30
K=19, L=3		
1	32	29
3	22	-25
5	17	-25
7	23	21
K=20, L=3		
0	26	20
K=0, L=4		
2	234	296
4	86	83
6	199	195
8	178	169
10	170	155
12	108	108
14	138	128
16	59	60
18	68	63
K=1, L=4		
1	219	218
3	78	86
5	165	168
7	196	208
9	187	177
11	74	67
13	79	79
15	42	49
17	56	52
K=2, L=4		
0	306	281
2	240	238
4	141	146
6	169	177
8	158	157
10	141	141
12	120	112
14	120	100
16	58	60
18	44	52
K=3, L=4		
1	186	171
3	238	236
5	202	201
7	127	134
9	88	93
11	118	119
13	115	109
15	92	85
17	40	48
K=4, L=4		
0	43	36
2	173	154
4	309	326
6	194	202
8	125	126
10	84	90
12	128	117
14	88	81
16	87	82
18	19	36
K=5, L=4		
1	153	134
3	263	262
5	173	170
7	103	102
9	73	79
11	128	133
13	83	79
15	106	89
17	49	61
K=6, L=4		
0	213	169
2	195	171
4	212	210
6	111	108
8	149	157
10	132	142
12	104	99
14	30	35
16	80	75
K=7, L=4		
1	208	194
3	196	179
5	116	113
7	110	120
9	139	151
11	128	133
13	47	53
15	47	49
17	51	61
K=8, L=4		
0	214	188
2	172	158
4	137	125
6	110	109
8	114	120
10	121	118
12	80	79
14	43	54
16	37	45
K=9, L=4		
1	199	183
3	113	105
5	132	127
7	128	136
9	121	132
11	70	77
13	76	78
15	36	48
K=10, L=4		
0	214	197
2	146	146
4	68	72
6	147	152
8	121	123
10	79	84
12	46	55
14	79	82
K=11, L=4		
1	162	147
3	70	77
5	116	115
7	120	117
9	73	80
11	35	44
13	90	88
15	48	56
K=12, L=4		
0	93	83
2	116	113
4	123	130
6	147	156
8	71	74
10	39	44
12	65	70
14	85	89
K=13, L=4		
1	69	73
3	127	123
5	129	131
7	78	85
9	30	36
11	43	54
13	69	74
K=14, L=4		
0	71	82
2	101	99
4	105	106
6	70	76
8	67	76
10	59	71
12	53	63
K=15, L=4		
1	92	95
3	100	93
5	40	45
7	52	62
9	75	81
11	66	73
K=16, L=4		
0	91	99
2	90	87
4	74	75
6	23	33
8	70	78
10	80	84
K=17, L=4		
1	51	65
3	78	79
5	51	56
7	32	48
9	50	63
K=18, L=4		
0	52	61
2	51	59
4	65	67
6	33	42
8	24	39
K=19, L=4		
1	48	52
3	40	55
5	54	70
K=20, L=4		
0	40	48
2	23	42
K=1, L=5		
1	23	-17
3	7	-10
5	22	22
7	36	34
9	41	-44
11	23	-29
13	23	19
15	24	22
K=2, L=5		
0	13	-6
2	19	-19
4	8	-7
6	52	56
8	11	4
10	61	-62
12	13	13
14	41	37
K=3, L=5		
1	18	9
3	8	-10
5	23	22
7	57	51
9	47	-50
11	23	-24
13	32	34
15	27	26
L=4, L=5		
0	26	9
2	14	-19
4	20	-29
6	18	14
8	11	3
10	27	-30
K=5, L=5		
1	34	25
3	9	-15
5	10	-17
7	20	12
9	27	22
K=6, L=5		
0	68	63
2	33	24
4	22	-28
6	37	-44
8	12	16
10	52	46
K=7, L=5		
1	10	-13
3	10	-10
5	20	-23
7	26	-27
9	55	52
11	13	11
13	36	-43
15	25	-28
K=8, L=5		
0	10	-3
2	42	29
4	45	35
6	26	-36
8	23	-24
10	44	39
K=9, L=5		
1	53	-65
3	51	37
5	48	43
7	23	-32
K=10, L=5		
0	56	-62
2	12	-1
4	59	56
6	32	29
8	23	-20
10	12	-13
12	11	11
14	21	17
L=11, L=5		
1	12	-5
3	12	-4
5	13	-9
7	13	-8
9	27	-35
11	11	-12
13	19	11
K=12, L=5		
0	28	14
2	12	-3
4	13	-11
6	46	40
8	42	37
K=13, L=5		
1	46	37
3	29	-34
5	33	-42
K=14, L=5		
0	45	40
2	13	-1
4	12	-30
6	12	7
8	27	24
K=15, L=5		
1	27	19
3	12	-19
5	11	-15
7	10	11
9	19	13
K=16, L=5		
0	25	20
K=17, L=5		
1	10	-20
3	10	8
5	20	16
K=18, L=5		
0	19	-32
2	8	1
4	34	33
K=19, L=5		
0	14	-0
K=0, L=6		
2	119	129
4	198	205
6	156	160
8	56	53
10	83	78
12	83	68
14	64	53
16	43	50
K=1, L=6		
1	130	133
3	182	210
5	156	159
7	85	79
9	85	85
11	125	111
13	108	92
15	73	70
K=2, L=6		
0	150	122
2	155	145
4	117	119
6	113	113
8	115	108
10	107	106
12	69	63
14	45	44
16	44	51
K=3, L=6		
1	200	175
3	114	106
5	94	99
7	125	133
9	134	134
11	91	85
13	56	52
15	42	47
K=4, L=6		
0	257	239
2	143	125
4	84	83
6	88	86
8	119	124
10	88	86
12	73	74
14	54	60
K=5, L=6		
1	189	159
3	99	86
5	120	117
7	146	149
9	108	109
11	73	68
13	66	67
15	46	48
K=6, L=6		
0	206	195
2	111	103
4	101	98
6	107	105
8	107	111
10	62	58
12	75	73
14	72	72
K=7, L=6		
1	139	119
3	107	102
5	111	118
7	107	115
9	65	66
11	51	55
13	72	71
15	45	60
K=8, L=6		
0	86	75
2	120	111
4	133	138
6	110	127
8	68	77
10	51	56
12	68	69
14	65	68
K=9, L=6		
1	65	69
3	134	138
5	116	123
7	64	72
9	51	51
11	64	65
13	59	59
K=10, L=6		
0	50	47
2	123	119
4	114	106
6	66	75
8	51	53
10	81	87
12	55	61
K=11, L=6		
1	89	95
3	111	113
5	71	75
7	53	60
9	84	92
11	77	78
K=12, L=6		
0	90	94
2	92	99
4	57	58
6	41	46
8	60	68
10	84	87
12	30	40
K=13, L=6		
1	90	95
3	63	68
5	54	57
7	55	66
9	71	81
11	43	54
K=14, L=6		
0	94	92
2	53	61
4	56	62
6	63	61
8	60	61
10	29	41
K=15, L=6		
1	68	67
3	44	55
5	65	74
7	59	66
K=16, L=6		
0	55	57
2	32	39
4	50	66
6	57	68
K=17, L=6		
1	41	50
3	36	47
5	36	58

Table 3. *Molecular parameters of thiourea* (Å)

	S–C	C–N	S–N	N–N	N–C–N	S–C–N
1	1·76	1·35	2·69	2·35	121°	120°
2	1·77	1·33	2·70	2·27	117°	122°
σ	0·02	0·02	0·02	0·03	2°	1°
TU	1·720	1·34	2·66	2·31	119°	120·5°

and 1·41 Å respectively (σ=0·03 Å). The four independent C–C–C angles in the benzene ring are 118·5°, 121·5°, 118° and 121·5° (σ=3°). Although these data are not very accurate a normal benzene ring is indicated. The carboxyl C–C and C=O bonds are 1·53 ± 0·03 Å and 1·25 ± 0·02 Å. The angles C–C–O and O–C–O are 118 ± 2° and 124 ± 3°. Because of the high standard deviations no meaningful departure from regularity can be claimed here either.

According to interatomic distances each benzoate ion is strongly hydrogen bonded to the surrounding amino groups belonging to the thiourea molecules. There are two different NH···O approaches. That of 2·92 ± 0·02 Å indicates a powerful hydrogen bond whereas the other of 3·03 ± 0·02 Å is within the range of O–H–N hydrogen bonds given by Pimentel & McClellan (1960).

Discussion of the structure

It is striking that the thiourea molecules involved in the shorter type of NH···O approach are the same molecules involved in the shorter Tl···S and S···S approaches. It thus appears as if only the 2·92 Å NH···O approach describes a hydrogen bond, whereas the 3·03 Å approach does not involve a hydrogen bond.* This means that hydrogen bonding to the anion entails a considerable modification of the electronic structure of a thiourea molecule. A satisfactory description is that the dipole moment of the thiourea is enhanced by the hydrogen bonding. This leads automatically to a stronger electrostatic interaction with the thallous ion and hence the short Tl---S distance. When this induction operates into neighbouring sulphur atoms the possibility of weak π-bonding between them can lead to the close S---S approach.

This effect was overlooked in the analysis of the $TlH_2PO_4.4TU$ structure (Verhoef & Boeyens, 1968) which is characterized by $(Tl\text{–}4TU)_n$ coordination columns of symmetry $4/m$. The sulphur atoms of thiourea molecules involved in hydrogen bonding are then diametrically opposed in the (001) sulphur squares. The π-bonding therefore does not occur and the sulphur squares appeared to be normal. Two different Tl---S distances were however observed (3·41 and 3·45 Å) but their significance was not appreciated. The thiourea molecules involved in the close Tl---S approaches are hydrogen bonded to the phosphate ion, d(NH---O) = 2·94 Å, and the others are not.

The effect is obvious in the present structure because only one end of the benzoate ion contains a polar group. Since there is no special interaction between the apolar end of the benzoate and the polar amino groups, only the polar end of a benzoate is surrounded by $-NH_2$ groups. It is impossible to arrange $(Tl\text{–}4TU)_n$ columns with $4/m$ symmetry in such a way that *all* amino groups are directed towards only one end of an anion situated in a channel among the columns. A different symmetry of the columns is required to induce such an arrangement. For this reason the coordination columns in the present structure have mm (or $2_1/m$) symmetry. The sulphur atoms of thiourea molecules involved in hydrogen bonding are now adjacent in the (001) sulphur squares and therefore favourably situated to interact by forming weak π-bonds.

The model which describes the thiourea complexes in terms of the close packing of anions and invariant coordination columns of symmetry $4/m$, except for small distortions, must therefore be revised. The problem is more general and best formulated in terms of the electrostatic interaction of the reaction species. Only when the anions can be approximated by point charges is the old model valid. In the case of more complicated anions however, their geometries also play a rôle and as demonstrated here the column is built up so as to interact most effectively with the polar parts of such an anion.

The deviation in $Tl_3PO_4.6TU$ from the familar Tl:S = 1:4 ratio can now also be explained since the interaction of isolated anions with long $(Tl^+.4TU)_n$ columns depends on the number of effective contacts. For a cation:anion ratio of 3:1 these contacts would occur on the average every 12 Å which is so inefficient that a column of a different geometry and composition, and compatible with the 3:1 ratio, is formed instead.

The fact that only very drastic conditions seem to cause the formation of coordination columns which are not of the $4/m$ type, indicates that this arrangement of sulphur atoms at the corners of a distorted Archimedean antiprism around the cation is energetically the most favourable. It even occurs when not favoured by stoichiometric relationships as in lead (II) salt complexes and complexes of the thallous salts of dibasic acids (Boeyens & Herbstein, 1967).

Conclusion

The details of this structure have completely changed current ideas about the stability of the ionic thiourea

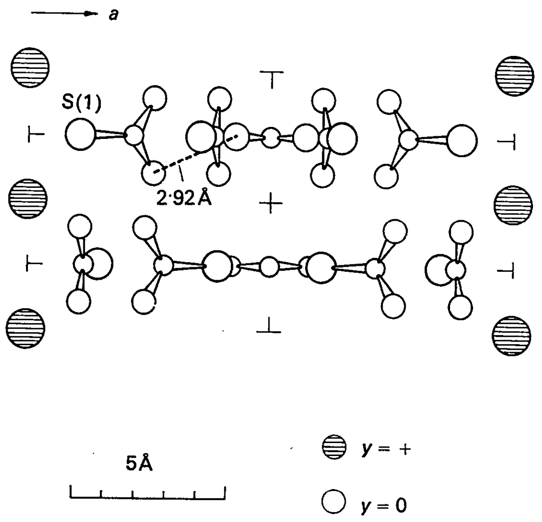

Fig. 2. (010) projection of the surroundings of a benzoate ion. The benzoate ion in the upper half of the diagram is viewed from its polar end and the benzoate ion in the lower half from its apolar end.

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* The interpretation of a similar 3·03 Å approach as a possible hydrogen bond in the structure of $CsF.4TU.2H_2O$ (Boeyens, 1968*a*) now appears to have been wrong.

complexes. It has been demonstrated that the very stable $(M^{+}.4\mathrm{TU})_n$ coordination column with symmetry $4/m$ is not an essential structural unit. A better criterion is that these complexes will form whenever any three-dimensional arrangement of ions and dipoles in the same crystal gives a higher intrinsically negative lattice energy than the sum of the lattice energies of the separate crystals. These quantities are exactly calculable and a programme is under way to investigate the electrostatic stability of various structure types by numerical methods.

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The Structure of Three Isomers $S_6(NH)_2$

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The three known isomers of $S_6(NH)_2$ were studied. Two-dimensional X-ray work showed one of the isomers, $S_6(NH)_2$ II with m.p. 153°C, to be identical with the compound $S_6(NH)_2$ studied by Weiss (*Z. anorg. chem.* (1960) **305**, 190). The four molecules in the orthorhombic unit cell with $a=7{\cdot}87$, $b=12{\cdot}86$, $c=7{\cdot}38$ Å lie at special positions m in space group *Pnma*. They contain eight-membered puckered rings of sulphur and nitrogen atoms (crown conformation) with the latter in the 1,5 positions.

The crystals of $S_6(NH)_2$ I (m.p. 130°C) are monoclinic with $a=8{\cdot}054$, $b=12{\cdot}522$, $c=8{\cdot}368$ Å, $\beta=114{\cdot}45°$, space group $P2/n$. The unit cell contains two independent pairs of molecules lying at special positions with symmetry 2. The crystal structure was determined from a three-dimensional Patterson synthesis and a difference synthesis. Refinement by anisotropic least-squares analysis of 1244 independent reflexions with non-zero intensity gave an index R of 0·048. The molecules are eight-membered rings in crown conformation. The NH groups appeared to be in the 1,4 positions. Average bond lengths and angles with e.s.d.'s for the individual values in parentheses are $\text{S–S}=2{\cdot}048\ (0{\cdot}006)$, $\text{N–S}=1{\cdot}724\ (0{\cdot}010)$ Å, $\angle\text{SNS}=119{\cdot}1\ (0{\cdot}5)$, $\angle\text{NSS}=110{\cdot}1\ (0{\cdot}4)$ and $\angle\text{SSS}=107{\cdot}3\ (0{\cdot}2)°$.

For $S_6(NH)_2$ III only preliminary X-ray work was done. Chemical considerations and comparison of the infrared and mass spectra of the three isomers very strongly indicated that $S_6(NH)_2$ III (m.p. 123°C, space group *Pbca*, $a=8{\cdot}18$, $b=12{\cdot}84$, $c=14{\cdot}06$ Å, $Z=8$ formula units) is cyclohexasulphur-1,3-diimide.

Introduction

From the reaction mixture of S_2Cl_2 and NH_3 several sulphur imides have been isolated: Goehring, Herb & Koch (1951) prepared a compound with formula S_7NH, Weiss (1959) obtained a solid with composition $S_6(NH)_2$ in addition to S_7NH and some other products, Tavs, Schulze-Steinen & Colchester (1963) and Heal (1963) showed by careful absorption chromatography that not only one, but three, compounds $S_6(NH)_2$ were formed during the reaction. Later, Heal & Kane (1964) succeeded in isolating two isomers with composition $S_5(NH)_3$. As all these sulphur imides obey the general formula $S_{8-x}(NH)_x$, it was supposed that they contained eight-membered rings as in S_8, with one or more of the sulphur atoms replaced by NH groups. A similar structure was assumed for $S_4(NH)_4$ which had been prepared by reduction of S_4N_4 by $SnCl_2$ in methanol (Meuwsen & Lösel, 1953). For some compounds, *e.g.* S_7NH (Weiss, 1960; Weiss & Neubert, 1965) and $S_4(NH)_4$ (Lund & Svendsen, 1957; Sass & Donohue, 1958), the hypothesis was confirmed by an X-ray study of the crystal structures. In both cases the shape of the ring is analogous to the crown shape observed in orthorhombic sulphur. In $S_4(NH)_4$ the ring appeared to consist of alternating sulphur and nitrogen atoms.

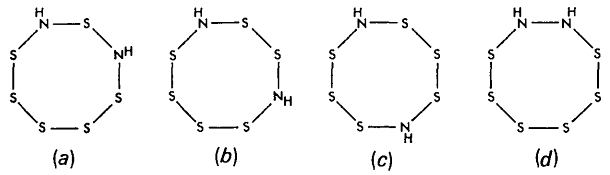

Fig. 1. Possible molecular structures for the isomers $S_6(NH)_2$.