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

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The three-dimensional structure of TlClO₃.4(SCN₂H₄) has been determined by means of data collected with an X-ray single-crystal diffractometer. After full-matrix least-squares refinement a discrepancy of 5.5% between observed and calculated structure factors for 1519 measured intensities was observed. The cations and anions were found to be completely segregated. The thallous ions occur along [001] in a linear chain which is surrounded by sulphur atoms arranged anti-prismatically around individual thallous ions. The amine ends of the thiourea molecules enclose the chlorate ions in elliptical channels parallel to [001]. The chlorine atom and the three oxygen atoms composing the chlorate ion lie at the apices of a distorted tetrahedron and no indications of hydrogen bonding have been observed.

Introduction

The ionic salt complexes of thiourea, with the $TICIO_3$ complex as the only exception, are characterized by fairly high symmetry (Boeyens & Herbstein, 1967). The geometry of the chlorate ion is undoubtedly responsible for the anomalous behaviour and the mechanism whereby it lowers the symmetry of the complex can only be determined through a structural study.

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Experimental

Crystals of the complex were obtained from an aqueous solution of its components. The crystals are monoclinic and the unit-cell dimensions as refined on a fourcircle Hilger & Watts diffractometer are: $a = 22 \cdot 037 \pm 0.011$, $b = 9.869 \pm 0.005$, $c = 8.201 \pm 0.004$ Å, $\gamma = 103.95 \pm 0.01^{\circ}$. The density calculated for four formula units per unit cell is 2.21 g.cm⁻³ compared with the measured density (Boeyens & Herbstein, 1967) of 2.20 g.cm⁻³. The condition limiting possible reflexions is: hkl for h+l=2n. The structure was solved successfully assuming the centrosymmetric space group B2/m which is consistent with the reflexion condition.



Fig. 1. Projection of the structure along [001]. Atoms represented by open and solid circles belong to molecules lying across the mirror planes at z=0 and $\frac{1}{2}$ respectively. Concentric circles represent mirrored pairs of either nitrogen or oxygen atoms which overlap in projection. Striped circles represent Tl atoms at $z \simeq \frac{1}{4}$ and $\frac{3}{4}$.

A needle-shaped crystal $(0.04^2 \times 0.084 \text{ mm})$ was used to collect 2784 intensities (the complete copper sphere) using Mo Ka (Zr filter) radiation and an ω -scan on the Hilger & Watts instrument. All the usual corrections as described recently (Roux & Boeyens, 1970) were applied and only the 1519 reflexions with intensities above significance level were given non-zero uniform weight in the final refinement (Dunning & Vand, 1969). All computer programs and scattering factor tables used in the analysis had been described before (Roux & Boeyens, 1969).

Determination and refinement of the structure

A three-dimensional Patterson synthesis was calculated on an IBM 360/65 computer. The Tl-Tl vectors were readily identified and from the other peaks in evidence the positions of Cl and S relative to Tl could be established. All available evidence indicated the thiourea molecules and chlorate ions to lie across the mirror planes at $z=0, \frac{1}{2}$ so that Tl atoms could be placed in any of the (e) or (g) fourfold positions, or their equivalent sets. The notation used here is that of *International Tables for X-ray Crystallography* (1965) for space group no. 12. Positions (g) which are of the type 00z are only allowed for $z\simeq \frac{1}{4}$. Inspection revealed that occupation of positions (e) would entail unrealistically short interatomic distances between neighbouring chlorate groups.

A Fourier synthesis with Tl in (g) gave a trial structure which could be refined directly. Full-matrix refinement of the atomic parameters and anisotropic temperature factors was considered complete when all parameter shifts were less than 0.1 of their estimated standard deviations. At termination the conventional R index was 0.055.

The final atomic and thermal parameters of the atoms in the asymmetric unit are listed in Table 1 and the observed and calculated structure factors on an absolute scale in Table 2; F(000) = 1064.

Description of the structure

An excellent view of the structure is provided by the projection along [001], shown in Fig. 1.

The main feature of the structure is the occurrence of infinite coordination columns of composition. Tl⁺.4 thiourea which lie along [001]. The interthallium distances within the column are not constant, but alternate between the two values 4.148 ± 0.003 and 4.053 ± 0.003 Å. There are four independent Tl–S distances of

Tl-S(1): 3.330) .
TI-S(2): 3.386	± 0.018 Å
TI-S(3): 3.431	}
Tl-S(4): 3.509	

The four sulphur atoms in the same mirror plane do thus not define a perfect square and this is also evident

		β_{23}	0	0	0	C	• c		0	0	105 (188)	21 (130)		148 (136)	- 191 (173)	- 221 (136)	Ć	-	0	0	c	>
		β_{13}	0	0	0	c	.	o	0	0	110 (79)	68 (68)		(69) 29	16 (86)	-52 (73)		- (0	0		>
		β_{12}	61 (3)	116 (21)	-4 (22)	(() 12		-18 (23)	-2 (19)	133 (80)	249 (71)	(07) 20	0/ (4)	64 (50)	280 (71)	20(52)		(60) 54	85 (79)	111 (90)	122 (85)	(00) 001
323)].	es.	β_{33}	1290 (12)	949 (78)	981 (81)	1032 (81)		1058 (81)	1207 (81)	2660 (379)	1515 (228)		(NET) SCOT	1139 (201)	1228 (227)	1193 (205)		(41 (203)	1046 (319)	1221 (359)	1155 (227)	(/ () () () ()
_{12.} + 2 <i>hlβ</i> ₁₃ + 2 <i>kl</i> J	en in parenthes	β22	(8) 462	776 (54)	897 (59)	CO0 (53)	((() 060	595 (50)	(6) (4)	939 (193)	(00) 2100			841 (125)	1408 (176)	768 (122)		347 (152)	408 (178)	1001 (246)		(677) 916
$11 + 1^2\beta_{33} + 2hk\beta_{11}$	viations are giv	β_{11}	2.57 (2)	158 (12)	151 (13)		(41) 002	237 (15)	146 (11)	210 (51)	30/ (36)		(15) 677	213 (31)	321 (41)	254 (34)		176 (46)	204 (52)	157 (10)		146 (4/)
$T = \exp\left[-(\hbar^2\beta)\right]$	Standard de	2	0.24708 (15)			> <	0	0			0.11121 (165)	(cor) ICI+I.0	0.13621 (154)	0-13884 (158)	0.14120 (177)		(701) 70001.0	0	C		2	0
				0 0 37666 (61)	(1c) ccc/7.0	(cc) 06007.0	0.92889 (54)	0.00558 (54)	0.67920 (18)	0.51640 (165)	(01) (40) (100)	0.01098 (140)	0.65697 (110)	0.50203 (112)	0.11435 (141)	(I+I) 24010	0.233// (112)	0.67515 (159)	0.63103 (176)		0.0013/ (210)	0-16855 (204)
		ډ	×	0	0-03622 (26)	0-49604 (27)	0.37220(27)	0-1-040 (20)	(7) (7) (7) (7)	(+7) (71) (72)	0.20381 (12)	0.19059 (60)	0-06109 (57)	0.20022 (56)	(00) 70960.0	(0/) / \$175.0	0.18726(60)	0.03373 (89)		(16) 11074.0	0.33531 (97)	0-17051 (93)
			i	=	(1)	§(2)			(4)		(1)	D(2)			(7)	N(3)	Z(4)			(7)	C(3)	C(4)

Table 1. Fractional coordinates and anisotropic thermal parameters ($imes 10^5$)

1 7 7	4 37 41 2 37 -44	6 119 -123 4 256 265	2 60 -62 0 38 42	H=5,K=-9 3 29 -23	10 37 -39 8 102 102	4 85 84 2 85 -87	3 62 -03 1 64 -61	6 63 -59 4 103 107	8 30 26 6 111 -118	8 45 50 6 63 -68 4 143 150	2 79 -77 0 142 137	2 82 -76 0 103 101 He18, Kal	H=22, K=-7 4 51 52
H=0,K=-13 0 44 49 H=0,K=-12 4 35 41 2 37 -44	0 56 67 K=0,K=13 0 40 49 H=1,K=-10 3 33 32	2 201 -214 0 317 333 H=2,K=0 8 83 95 6 111 -130	Hc4,K=-11 4 47 51 2 50 -55 0 94 101 H=4,K=-10	1 44 -44 H=5,K=-7 7 34 -34 5 30 -28 3 54 -53	4 186 184 2 171 -174 0 428 4 37 H=6,K=2	U 88 87 H=8, K=-8 8 51 48 6 44 -44 4 140 138	3 42 -41 1 22 -19 k=9, K=-2 5 43 47	A 77 -77 0 107 100 H=10, K=7 6 50 -46 4 78 75	2 201 -210 0 86 89 H=12, K=2 10 34 -35	2 95 -102 0 123 131 H=14, K=-1 8 40 39 6 81 -86	8 53 58 6 27 -32 4 118 118 2 59 -63 0 165 167	8 32 35 6 33 -39 4 72 70 2 76 -73 0 108 104	H=22, K=-6 4 46 41 2 48 -45 0 34 34 H=22, K=-5
0 63 67 H=0,K=-11 4 84 93 0 96 100	1 34 33 H=1,K=-8 5 34 31 3 35 36	4 225 258 2 210 -244 0 245 282 H=2,K=1	6 68 -73 4 45 47 2 111 -110 0 43 42	1 50 -52 H=5,Kn-6 7 48 -43 1 73 -67	10 38 -39 8 56 49 6 151 -147 4 181 185 2 245 -249	2 65 -66 0 138 134 H=8, K=-7 8 46 44	3 64 65 H=9, K=-1 3 40 -45 1 38 45 H=9, K=0	2 80 -81 0 107 107 H=10, K=8 6 39 -43 4 52 56	8 47 51 6 82 -82 4 86 88 2 154 -156 0 169 168	4 77 76 2 151 -163 0 133 135 H=14, K=0	H=16, K=-2 8 46 43 6 52 -53 4 92 96	H=18, K=2 6 73 -70 4 37 34 2 116 -114	6 33 -34 2 62 -59 0 54 49 8=22, K=-4
R=0, K=-10 6 41 -45 4 64 67 2 78 -79	1 25 28 H=1,K=7 3 59 54 3 67 61	10 56 -51 8 74 69 6 158 -152 4 196 191 2 101 -298	H=4, K=-9 6 71 -70 4 71 75 2 118 -116 0 78 75	H=5,K=-5 7 44 45 5 48 40 1 137 131	0 115 115 H=6,K=3 8 100 94 6 68 -67	6 80 -78 4 65 60 2 164 -161 0 146 143	7 31 -37 1 57 -61 H=9, K=1 3 51 -54	4 52 50 2 75 -75 0 81 84 H=10, K=9 4 63 68	H=12, K=3 8 31 32 6 92 -96 4 71 67	8 41 41 6 74 -79 4 126 131 2 114 -122	2 94 -100 0 124 132 H=16, Km-1 8 48 51	0 36 34 Hal8, K=3 6 51 -51 2 95 -97	6 37 -35 4 48 42 2 61 -54 0 48 41
H=0,K=-9 5 75 -75 4 43 41 2 133 -134	H=1,K=-6 1 22 21 ft=1,K=-5 5 35 33	0 271 265 H=2,K=2 10 76 -71 8 48 40	H=4,K==8 8 63 67 6 40 -38 4 114 113	7 35 -30 3 33 -30 1 52 -51 H=5,K=-3	4 193 186 2 143 -144 0 326 327 H=6,K=4	10 33 -34 8 47 44 6 91 -89 4 103 106	1 28 27 Har9, K=2 7 44 42 5 49 46	2 44 -40 0 82 83 H=10, K=10 2 44 -19	2 172 -172 0 104 106 H=12, K=4 8 42 36 6 71 -73	H=14, X=1 8 54 61 6 45 -49 4 137 141	6 45 -43 4 114 116 2 78 -78 0 146 147 H=16, Xa0	L 71 70 H=18, K=4 6 44 -42 4 53 50 2 73 -68	H=22, K=-3 4 70 65 2 39 -30 0 73 72 H=22, K=-2
0 85 80 N≈0,K¤~8 8 60 60 6 46 -44	1 56 53 Sm1,Ka=4 3 22 -21 1 24 21	6 210 -193 4 91 88 2 422 -465 0 152 133 Re2.Ke3	2 81 -80 0 202 202 H=4,K=-7 8 42 40 4 95 -96	7 25 -25 3 63 -58 1 32 -30 H=5,K=-2 5 44 46	6 57 -51 4 203 192 2 113 -108 0 297 291	2 158 -158 0 160 160 H=8, K=-5 8 58 59 6 91 -91	H#9, R=3 5 84 80 3 116 114 1 59 57	H=10, K=11 0 37 45 H=11, K=-9 1 31 29	4 86 83 2 128 -132 0 108 112 H=12, K=5	2 77 -80 0 168 173 H=14, K=2 8 46 48	8 55 54 6 40 -41 4 83 83 2 89 -90	0 57 53 R=18, K=5 6 37 -35 4 49 50	4 08 05 2 72 -59 H=22, K=-1 6 52 -50
4 112 111 2 87 -87 0 181 182 H=0,K=-7 8 54 52	7 37 -32 3 34 -34 1 62 -57 H=1,K=-2	10 41 -45 8 98 89 6 115 -105 4 168 156	4 121 124 2 153 -152 0 99 99 He4,K=6	3 42 41 1 47 49 H≈5,K=-1 7 37 -48	H=6,K=5 6 124 -121 4 113 114 2 198 -193	4 129 138 2 177 -177 0 177 170 H=8, K=-4	H⊪9, K∞4 3 49 -47 1 32 -29 H⊮9, K⊽5 5 41 39	H=11, K=-8 3 32 -27 1 50 -46 H=11, K=-7 7 1 27	6 56 -52 4 101 100 2 91 -87 0 118 117	4 79 80 2 125 -124 0 156 153 H=14, K=3	Hel6, K=1 8 50 50 6 44 -37 4 111 110	2 53 54 0 51 48 He18, Ke6 2 60 -57 0 49 45	2 90 -84 0 36 27 Hs22, Ke0 4 66 64 0 105 93
6 80 -80 4 122 124 2 139 -137 0 148 142	5 31 29 3 36 -30 1 130 115 H=1,K=-1 7 28 -10	2 239 -224 0 390 362 H=2,K=4 10 32 -30 8 101 93	8 50 51 6 98 -98 4 131 127 2 174 -170 0 185 180	3 62 57 1 112 -115 H=5,K=0 5 30 12	H=6,K=6 8 52 51 6 74 -71 4 125 125	8 83 83 6 70 -70 4 149 152 2 143 -150 0 293 299	3 39 38 1 48 47 H=9, K=6 5 50 50	5 35 -39 3 71 -67 1 63 -60 H=11, K=-6	H=12, K=6 6 70 -71 4 66 62 2 110 -108	8 52 50 6 46 -44 4 124 123 2 72 -70	2 71 -72 0 141 142 H=16, K=2 8 42 44	H=18, K=7 2 48 -56 0 35 26 H=18, K=8	H=22, K=1 4 62 58 2 28 -26 0 85 77
H=0,K=-5 \$ 47 47 6 109 -106 4 143 142 2 176 -168	3 43 -36 1 66 -46 H=1,K=0 3 25 -25	6 81 -76 4 195 184 2 177 -169 0 341 325	Hm4,K=-5 10 35 -38 8 54 52 6 125 -121	1 71 73 H=5,K=1 7 36 -30 1 36 -25	2 128 -124 0 148 148 H=6,K=7 8 52 57	H=8, K=-3 8 68 71 6 86 -95 4 199 215	3 54 51 1 61 58 H=10, K=-13 2 37 -45 H=10, K=-12	1 23 -21 H=11, K=-5 3 39 -37 H=11, K=-4	H=12, K=7 6 43 -42 4 57 60 2 72 -73	0 144 142 H=14, K=4 8 43 48 6 34 -36 4 106 103	6 33 -37 4 130 128 2 50 -52 0 121 117 H=16, K=3	4 34 42 0 49 54 H=19, K=-8 3 34 -31 H=19, K=-5	H=22, K=2 2 54 -54 0 38 34 H=22, K=3 4 51 46
0 158 146 H=0,K=-5 10 37 -43 8 66 64	1 42 27 H=1,K=1 5 44 38 3 45 31 1 56 22	H=2,K=5 10 45 -49 6 162 -152 4 126 124 2 249 -245	4 151 143 2 221 -216 0 156 150 Hm4,Kn=4 10 34 -35	H=5,K=2 7 34 -34 3 59 -58 1 66 -66 H=5,K=3	4 125 123 2 75 -79 0 157 154 H=6,K=8	2 152 -162 0 190 201 H=8, K=-2 10 36 -39 8 78 82	2 51 -54 0 43 46 Halo, Kn-11 6 39 -46	3 81 -82 H-11, Ka-3 7 66 -70 5 59 -61	0 90 87 H=12, K=8 6 33 -35 4 47 48	2 70 -66 0 141 138 H=14, K=5 6 35 -40 4 83 79	6 61 -65 4 45 43 2 114 -112 0 80 79	1 31 -28 H=19, K=-3 3 51 -47 1 31 -31	2 33 -30 0 56 52 H=22, K=4 0 62 61
4 125 122 2 226 -215 0 232 224 H=0,K=-4	H=1,K=2 7 69 -66 3 67 50 1 202 -175	0 80 75 H=2,K=6 10 35 -38 8 49 49	8 82 75 6 109 -100 4 201 192 2 189 -185 0 276 267	5 36 37 3 21 18 1 60 58 H=5,K=4	6 78 -77 4 39 35 2 132 -137 0 73 76 H+6.K-9	6 94 -97 4 142 151 2 182 -195 0 296 311	0 33 36 H=10, K=-10 6 49 -49 4 36 34	3 81 -89 1 135 -141 H=11, K=-1 5 29 37	0 70 73 H=12, K=9 6 39 -45 2 70 -73	2 74 -72 0 108 108 H=14, K=6 8 40 37	6 41 -39 4 78 80 2 69 -64 0 95 90	5 31 28 3 31 28 1 40 42 H=19, K=0	H=22, K=5 4 34 36 0 34 38 H=23, L=-2 1 31 26
8 83 78 6 113 -106 4 250 242 2 167 -162 0 229 219	9 38 35 7 54 49 5 35 52 1 198 175	6 102 -104 4 99 94 2 192 -190 0 157 156 H=2,K=7	H=4,K=-3 10 49 -49 8 95 90 6 109 -102	5 72 -65 3 123 -219 1 99 -95 H=5,K=5	6 59 -55 4 49 51 2 94 -96 0 67 67	8 86 98 6 58 -71 4 206 235 2 120 -139	2 89 -89 0 69 67 H=10, K=-9 6 67 -65	1 34 40 H=11, K=0 7 48 -53 5 43 -46	H=12, K=10 2 42 -45 H=13, K=-10 3 30 -27 H=13, K=-8	6 36 -33 4 82 60 2 65 -62 0 106 106 Hal4, Ka7	H=16, K=5 8 35 36 4 77 75 2 51 -46 0 103 100	3 36 -26 1 37 -39 He19, K=1 1 27 25 He19 K=3	H=24, K=-9 2 39 -39 H=24, K=+8 2 53 -44 H=24, K==7
H=0,K=-3 8 127 122 6 68 -61 4 270 255	H=1,K=4 5 46 45 3 39 31 1 57 53	8 72 74 6 44 -40 4 147 147 2 80 -81 0 218 217	4 132 123 2 266 -255 0 394 382 H=4,Ks-2 10 70 -77	5 48 -40 3 96 -94 1 49 -39 H=5,K=6 5 19 14	6 43 -44 4 43 45 2 70 -72 0 50 58	0 273 313 H=8, K=0 8 80 89 6 67 -77 4 274 311	2 105 -103 0 62 61 H=10, K=-8 8 36 40	3 72 -77 1 83 -85 H=11, K=2 5 65 66 3 84 83	1 27 -18 H=13, Km-7 5 33 -30 3 55 -55	6 49 -46 4 43 43 2 82 -78 0 46 44	H-16, K=6 6 48 -52 2 89 -90 0 38 38	1 30 -26 H=20, K=-11 2 36 -33 H=20, K=-10	4 39 40 0 61 56 H=24, K=-6 2 41 =35
2 144 -134 0 459 436 H=0,K=-2 10 55 -48 8 80 70	5 26 27 3 24 23 H=1,K=6 7 51 48	H=2,K=8 6 71 -72 4 106 106 2 113 -114	8 28 22 6 208 -217 4 75 76 2 401 -421 0 81 70	3 40 35 H=5,K=7 3 39 -38 1 41 -31	H=6,K=11 2 57 -61 0 37 42 H=6,K=12	2 73 -87 0 214 242 H=8, K=1 10 37 -38	6 51 ->4 4 77 78 2 100 -101 0 115 113 H=10, K=-7	1 79 77 H=11, K=3 5 27 -24 3 63 -61	H=13, K=-5 5 53 54 3 69 71 1 39 42	4 53 53 2 43 -43 0 50 57 H=14, K=9	4 61 58 2 34 -38 0 57 54 He16, Ke8	4 34 38. 0 39 45 H∋20, K≡-9 4 41 44 0 40 38	0 49 44 H=24, K=-5 6 36 -39 2 71 -62 H=24, K=-4
6 157 -144 4 224 211 2 276 -264 0 284 265	5 66 63 3 47 40 1 124 120 H=1,K=7 5 35 33	H=2,K=9 6 49 -51 4 73 76 2 86 -88 H=2,K=10	H=4,K=-1 10 52 -62 8 47 50 6 164 -179	H=5, K=6 3 33 -32 1 44 -43 H=6, K=-13 0 38 42	H=7,K=-10 3 39 -39 H=7,K=-9 5 42 41	8 70 74 6 102 -105 4 135 141 2 210 -220 0 243 252	8 42 47 6 60 -62 4 100 98 2 105 -103	H=11, K=4 3 36 -31 H=11, K=5 3 30 -31	H=13, K=-4 5 25 -24 3 58 -60 1 42 -41	2 42 -42 0 49 49 H=14, K=10 2 47 -51	4 39 43 0 70 70 H=16, K≈9 0 34 39 H=17 K=6	H=20, K=-8 2 64 -58 0 44 41 H=20, K=-7	4 50 47 0 74 66 Ha24, K=-3 4 61 55
10 42 -35 8 94 87 6 145 -131 4 289 266	3 37 33 1 26 26 K=1,K=8 3 26 -23	4 76 83 2 51 -54 0 77 95 H=2,K=11	4 100 112 0 146 159 H=4,K=0 10 34 −36 8 77 83	He6,Km-12 4 64 75 0 74 76 H=6,Km-11 4 68 68	3 51 47 1 43 42 H=7,K ≫-8 5 31 32 3 33 29	H=8, K=2 10 34 -27 8 91 86 6 74 -73	H=10, K=-6 6 107 -112 4 100 101 2 173 -173	He11, K=8 5 37 -36 3 61 -59 1 43 -38 He12, Ke-13	7 33 36 5 46 50 3 25 29 1 84 90	3 28 26 1 36 35 H=15, K=-6 5 28 29	1 32 27 Hal7, K=-5 1 38 41 Hal7, K=-4	2 36 -28 0 73 71 H≈20, K⇒-6 4 61 62	H=24, K=-2 4 37 33 2 46 -40 0 33 39
2 260 -245 0 288 271 R=0,K=0 8 212 205 6 56 42	5 34 31 1 37 38 H=2,K=-13 2 43 -60	2 39 -43 0 60 86 H=2,K=12 4 34 40	6 109 -124 4 215 248 2 188 -218 0 257 300 H=4,K=1	2 42 -46 0 82 87 H=6,K=-10 6 42 -44	1 32 34 H=7,K=-6 5 62 61 3 72 70	2 141 -140 0 304 301 H=5, K=3 8 84 82	0 49 44 H=10, K=-5 8 77 74 6 50 -45 4 172 170	2 42 -46 H=12, Km-12 2 39 -43 0 43 37 H=12 Km-11	H=13, K=-1 5 24 27 1 55 57 H=13, K=0 7 32 -33	3 25 24 1 45 42 Hal5, Km-5 5 42 40 3 38 35	7 38 -37 5 33 -34 3 58 -58 1 66 -67 H=17, K=0	2 49 -42 0 75 68 Ha20, K=-5 6 61 -61 2 117 -110	H=24, K=-1 4 46 39 2 33 -27 0 78 63 H=24, K=0
4 301 315 2 59 38 H=0,K=1 10 38 -35	H=2, K=-12 4 36 47 2 47 -49 0 49 51 H=2, K=-11	0 57 73 H=3,K=-8 3 39 -38 1 36 -33 H=3,K=-7	10 77 -77 8 35 32 6 219 -216 4 50 46 2 452	4 64 67 2 75 -77 0 87 87 H=6,K=-9 8 36 40	Hm7,K=-5 7 32 35 5 57 57 3 43 42	6 67 -62 4 183 178 2 129 -129 0 265 261 H=8, K=4	2 89 -86 0 252 243 H=10, K=-4 8 75 76	4 53 51 2 47 -51 0 40 42 H=12, K=-10	3 29 -35 1 52 -53 H=13, K=1 3 25 -24	1 45 48 Hal5, Ka-4 5 33 31 3 43 40	3 31 -33 H=17, K=2 5 40 39 3 43 42	0 38 27 H=20, K=-4 6 41 -40 4 66 59	4 68 60 0 60 49 H=24, K=1 4 52 48
6 145 -131 4 287 266 2 258 -245 0 287 271	6 36 -41 4 44 46 2 64 -72 0 97 66.	5 41 -33 3 74 -70 1 45 -43 H=3,K=-6	0 98 83 H=4,K=2 10 61 -62 8 37 38	6 50 -49 4 76 77 2 88 -91 0 126 122 H=6 Km=8	1 99 98 H=7,K⇒-4 5 49 50 3 43 42 1 61 59	8 71 67 6 69 -66 4 158 150 2 133 -127	4 161 163 2 121 -123 0 224 230 H=10, K=-3	6 46 -48 2 87 -86 0 51 56 H=12, K=-9 8 22 30	H=13, K=3 3 37 -32 H=13, K=4 7 60 -57	H=15, K==3 3 44 -47 H=15, K==2 5 65 71	H=17, K=5 5 40 42 3 44 44 1 49 48	2 65 63 H=20, K=-3 4 39 44 2 74 -69	H=24, K=2 2 48 -44 0 36 32 H=24, K=3
H=0,K=2 10 55 -48 8 79 70 6 158 -144 4 226 211	6 62 -66 4 35 43 2 107 -108 0 56 58	3 59 -56 1 45 -41 H=3,K=-5 7 56 -53	6 181 -175 4 141 129 2 333 -326 0 151 156 H=4.K=3	8 52 54 6 53 -54 4 96 97 2 103 -105	H=7,K=-3 1 23 -18 H=7,K=-2 5 31 32	H=8, K=5 8 51 53 6 79 -76 4 121 117	10 35 -42 8 52 56 6 95 -100 4 94 102 2 189 -203	6 42 -43 4 57 58 2 81 -78 0 89 83	5 43 -43 3 67 -63 1 101 -100 H=13, K=7 3 36 -37	3 88 91 1 62 66 H=15, K=-1 5 31 31 3 36 36	H=18, K=-12 2 39 -46 H=18, K=-13 2 44 -43 H=18, K=-10	0 97 96 H=20, K=-2 6 63 =61 2 112 -105 0 41 38	2 40 -39 H=24, K=4 4 39 38 0 59 57 H=26, K=9
2 273 -264 0 282 265 H=0,K=3 8 129 122	H=2,K=-9 6 75 -76 4 67 68 2 116 -119 0 71 75	5 39 -32 3 56 -48 1 102 -95 H=3,K=-4 7 44 -42	8 69 62 6 133 -131 4 227 221 2 213 -212 0 141 -40	0 150 148 H=6,K=-7 8 66 62 6 56 -55 4 137 139	1 112 116 H=7,K==1 7 43 42 5 52 60	2 130 -131 0 158 160 H=8, K=6 8 38 38 6 81 -76	0 210 220 H=10, K=-2 8 65 71 6 79 -81	6 45 -41 4 89 90 2 70 -70 0 118 112	1 35 -35 H=14, X=-13 O 39 49 H=14, K=-12	H=15, K=0 5 56 -52 3 100 -100 1 40 -42	4 33 34 2 47 -42 0 38 36 H=18, K=-9	H=20, K=-1 6 59 -62 4 54 47 2 95 -89	2 36 -34 H=26, K=-7 0 41 35 H=26, K=-5
6 69 -61 4 273 255 2 146 -134 0 459 436 H=0.K=4	H=2,K=-8 8 39 42 6 71 -73 4 94 91	1 76 -69 H=3,K=-3 7 43 -39 3 37 -30	H=4,K=4 10 46 -44 8 67 66 6 122 -115	2 98 -96 0 197 196 H=6,K=-6 10 40 -42 6 112 -129	1 141 146 H=7,K=0 7 43 -49 1 84 -87 H=7 K=1	4 86 87 2 132 -133 0 114 118 H=8, K=7	4 162 175 2 147 -159 0 211 229 Ho10, Ka-1 8 50 60	H=12, K=-7 6 70 -69 4 61 58 2 130 -130 0 99 96	H=14, K=-11 4 43 45 2 33 -33 0 70 68	H=15, K=1 3 26 27 H=15, K=2 5 31 36 3 63 65	0 37 32 H=18, K=-8 6 38 -45 4 35 35	H=20, K=0 6 53 -55 4 28 25 2 107 -98	2 33 -39 Ho26, K=-4 2 34 -29 0 46 39 H=26, K=-3
8 84 78 6 115 -106 4 247 242 2 165 -163 0 727 219	2 126 -130 0 123 118 H=2,K=-7 8 62 63 6 35 -56	H=3,K=-2 5 31 -29 3 111 -101 1 17 2	4 118 113 2 230 -225 0 242 229 H=4,K=5 10 43 -43	4 93 91 2 227 -220 0 81 75 H=6,K=-5	7 38 -42 5 62 -63 1 84 -83 H=7,K=2	6 41 50 6 43 -43 4 95 96 2 81 -82 0 139 140	6 96 -109 4 120 139 2 171 -198 0 170 195	H=12, K=-6 8 50 50 6 58 -57 4 103 101	H=14, K=-10 4 65 69 2 37 -33 0 72 70 H=14 K=-9	H=15, K=3 3 27 -28 1 26 -28 H=15, K=6 1 10 29	2 75 -71 0 33 34 H=18, Ke-7 6 32 -27 4 57 56	0 58 46 H=20, K-1 6 39 -40 4 57 53 2 72 -63	4 50 44 0 57 55 H=26, K=-2 2 51 -42
H=0,K=5 10 38 -43 8 69 64 6 113 -106	4 162 160 2 102 -98 0 199 195 H=2,K=-6 10 42 -46	H=3,K=-1 5 48 47 3 43 34 1 43 32 H=3,K=0	8 49 41 6 124 -120 4 110 108 2 219 -216 0 137 137	8 60 60 6 104 -102 4 123 119 2 198 -192	3 49 48 1 45 44 H=7,K=3 1 42 -41	H=8, K=8 8 35 33 6 45 -46 4 79 80 2 74 -76	10 34 -45 8 54 58 6 99 -108 4 76 88	0 163 158 H=12, Kn-5 8 45 46 6 77 -77	6 33 -35 4 70 64 2 55 -55 0 82 79	H=16, K=-12 0 42 43 H=16, K=-11 2 32 -35	2 57 -52 0 91 87 H=18, K=-6 6 32 -35 4 56 52	0 67 62 H=20, K=2 6 42 -42 4 46 37	6 35 -33 2 47 -53 H=26, K=0 4 43 41
4 126 122 2 224 -215 0 231 224 R=0, K=6 8 51 47	8 53 52 6 114 -106 4 82 76 2 229 -219	2 25 -18 1 29 -18 H=3,K=1 5 22 -17	H=4,K=6 10 38 -40 8 50 48 6 100 -94	0 218 218 Hm6,K=-4 8 90 83 6 89 -89	H=7,K=4 3 35 -34 1 21 18 H=7,K=5 3 23 18	0 94 95 H=8, K=9 6 50 -54 4 52 60 2 73 79	2 219 -230 0 199 214 H=10, K=1 8 52 54 6 101 -101	4 100 97 2 142 -142 0 134 133 H=12, K=-4 8 15 38	H=14, K=-8 6 34 -34 4 92 85 2 58 -58 0 101 95	H=16, K=10 4 39 44 2 48 -47 0 53 47	2 71 -70 0 98 88 H=18, K=-5 6 35 -42	0 55 52 H=20, K=3 6 51 -52 2 88 -86	0 51 48 H=26, K=1 2 43 -39 0 34 18 H=26, K=2
6 111 -106 4 144 142 2 172 -168 0 154 146	0 183 178 H=2,K=-5 10 48 -49 8 68 61 6 122 -118	3 118 -103 1 61 43 H=3,K=2 5 65 59 3 58 52	4 50 79 2 181 ~180 0 165 160 He4,Ke7 8 58 59	2 175 -170 0 264 256 H=6,K=-3 10 35 -45	1 37 5 H=7,K=6 5 51 42 3 46 40	0 42 46 H=8, K=10 4 58 60 0 88 97	4 160 172 2 155 -161 0 161 170 Halo, Ka2	6 90 -96 4 98 103 2 160 -163 0 122 124	H=14, K=-7 6 54 -49 4 83 86 2 82 -79 0 100 08	H=16, Kn-9 4 41 41 2 53 -52 0 89 83 9-16 8-9	4 67 63 2 75 -69 0 94 93 Hol8, K=-4 6 53 -54	H=20, K=4 4 64 60 2 34 -23 0 79 77 H=20, K=5	2 49 -46 H=28, K=-7 0 47 40 H=28, K=-5
8 56 52 6 80 -80 4 121 124 2 137 -137	4 104 101 2 238 -231 0 232 223 H=2,K=-4	1 86 84 H=3,K=3 5 23 20 3 24 -8	6 55 -50 4 121 118 2 104 -104 0 176 173	8 31 27 6 171 -174 4 185 186 2 259 -271 0 50 41	H=7,K=7 5 32 28 1 63 61 H=7,K=10	H=8, K=11 4 38 47 0 67 65 H=9, K=-9 5 36 31	8 34 34 6 134 -133 4 63 61 2 245 -250	Hal2, Ke-3 8 30 36 6 104 -111 4 109 116 2 169 -180	H=14, K=-6 6 69 -66 4 34 34 2 141 -138	6 51 -49 4 41 42 2 82 -78 0 67 59	4 67 65 2 93 -91 0 73 70 H=18, K=-3	4 36 40 2 35 -33 0 63 63 H=20, K=6	2 36 -31 H=28, K=4 0 44 38 H=28, K=-3 2 32 -20
0 145 142 H=0,K=8 8 57 60 6 43 -44 4 115 111	6 72 -71 4 275 270 2 127 -120 0 294 28	H=3,K=4 7 29 -27 1 27 -19 H=3,K=5	8 36 38 6 56 -58 4 118 115 2 81 -85	H=6,K=-2 10 46 -55 8 66 63 6 130 -140	5 36 39 3 42 42 1 45 49 Hn8, E-1 3	3 31 28 1 29 26 H=9, K=-8 5 35 40	0 107 113 H=10, K=3 8 36 38 6 102 -101 4 144 142	0 84 93 H=12, K=-2 10 37 -39 6 118 -122 4 93 100	0 116 -212 H=14, K=-5 8 36 36 6 63 -64 4 118 118	H=16, K=-7 6 53 -55 4 60 60 2 93 -87 0 56 54	6 43 -41 4 100 100 2 62 -61 0 98 94	H=20, K=7 0 35 44 H=21, K=-8 3 30 -23	H=28, K=-2 2 46 -43 H=30, K=0 0 48 40
2 90 -67 0 177 182 H=0,K=9 6 75 -74	H=2,K=-3 8 99 9 6 111 -10 4 239 22 2 200 -18	7 42 -43 1 3 23 -22 7 1 76 -73 4 H=3,K=6 9 3 51 -44	0 110 108 H=4,K#9 6 70 -73 2 125 -129 0 55 63	2 283 -303 0 230 247 H=6,K=-1 8 87 91	0 33 39 H=8, K=-12 4 53 59 0 69 75	3 48 25 1 67 64 R=9, K=-7 5 30 -26 3 52 -52	2 160 -159 0 114 110 H=10, K=4 8 43 43 6 90 -90	2 190 -206 0 94 97 R=12, Ke-1 8 48 51	2 97 -97 0 106 103 Hal4, Ka-4 6 81 -86	R=16, K==6 8 37 41 6 31 = 35 4 102 97	H=18, K=-2 8 41 43 6 40 -38 4 77 74 2 71 -72	H=21, K=-3 5 30 33 3 40 38 1 42 36 H=21, K=4	
4 34 41 2 132 -134 0 83 80 B=0,K=10 6 45 -45	0 353 32 H=2,K=-2 10 59 -5 8 63 6	R=3, K=8 7 43 -40 7 5 34 -30 1 3 49 -48	H=4,K=10 6 35 -39 4 51 60 2 65 -67	6 87 -100 4 200 226 2 155 -178 0 317 350 H=6,K=0	H=8, K=-11 4 64 68 2 35 -39 0 87 89	1 33 -31 H#9, K=-6 3 22 -19 H=9, K=-5 5 73 40	4 110 108 2 147 -147 0 118 120 H=10, K=5	6 89 -96 4 77 84 2 180 -195 0 166 180 H=12, K=0	2 158 -164 0 105 105 H=14, K=-3 10 34 -36	2 58 -53 0 118 117 H=16, K=-5 6 62 -64 4 70 70	0 125 126 H=18, K=-1 6 71 -70 4 57 55	3 32 -33 H=22, K=-11 O 42 38 H=22, K=-10	
4 63 67 2 80 -79 0 82 86 Rz0,Kall 4 84 01	6 174 -16 4 146 13 2 357 -34 0 210 20 Hez, Rm-1	9 H=3,K=9 9 3 38 -33 1 1 34 -29 H=4,K=-13	H=4,K=11 4 40 49 2 51 -58 0 47 51	8 85 92 6 91 -100 4 174 192 2 190 -220	6 55 -57 4 41 44 2 88 -92 0 62 65	3 95 94 1 49 49 H=9, K=-4 7 34 -36	8 31 30 6 98 -94 4 27 21 2 192 -186 0 117 113	8 37 43 6 97 -103 4 96 99 2 170 -184	8 43 46 6 71 -74 4 59 59 2 148 -155 0 162 167	2 109 -107 0 80 78 H=16, K=-4 8 36 45 6 47 42	2 118 -117 0 55 51 H=18, K=0 8 33 35 6 52 -45	H=22, K=-9 2 39 -39 H=22, K=-8 2 39 -38	
0 91 100 -0,K-12	8 99 89	2 55 -72 H=4,K=-12	He4,K=12 2 59 -70	H=6,K=1	6 56 -55	, , -32	H=10, K=6	H=12, K=1	R=14, K==2	4 99 100	1 * 16 15	0 54 45	·

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

Table 3. Dimensions of the thiourea group

	S-C	C-N	N-N	N-C-N
1	1·72 Å	1·30 Å	2·23 Å	118°
2	1.72	1.33	2.28	118
3	1.70	1.34	2.32	120
4	1.73	1.31	2.26	119
σ	0.02	0.05	0.03	2.0
UC TU	1.746 ± 0.008	1.349 ± 0.003		116.7 ± 0.2
TU in CC	1.76 ± 0.02	1.30 ± 0.04		120.4 ± 2.6

from the different S–S–S angles of 94.6, 91.2, 88.8 and 85.4° at S(1), S(2), S(3) and S(4) respectively. These slight distortions are related to nearest-neighbour approaches between nitrogen and oxygen atoms:

N(1)-O:	2.996	
N(2)-O:	3.094	± 0.02 Å
N(4)-O:	3.105	

Although no attempt was made to locate hydrogen atoms, these values all appear to be too long to represent hydrogen bonds (Verhoef & Boeyens, 1968).

The dimensions of the four independent thiourea molecules (TU) are summarized in Table 3 together with the dimensions for uncoordinated thiourea (UC) (Elcombe & Taylor, 1968) as well as for thiourea in a typical coordination complex (CC), *viz.* with cadmium formate (Nardelli, Gasparri & Boldrini, 1965).

The geometry of the chlorate ion is also as expected. The actual parameters are:

Cl–O	0-0	O-Cl-O
1·449 <u>+</u> 0·015 Å	2·318 ± 0·027 Å	$106.2 \pm 1.1^{\circ}$
1.454 ± 0.018	2.354 ± 0.022	108.3 ± 0.8

giving average dimensions: $Cl-O = 1.45 \pm 0.02$; $O-O = 2.34 \pm 0.025$ Å; $O-Cl-O = 107 \pm 1$; $O-O-O = 60.0 \pm 1^{\circ}$.

Discussion of the structure

It was pointed out before (Verhoef & Boeyens, 1969) that in the absence of complicating factors such as hydrogen bonding, the structures of all ionic thiourea complexes can be described in terms of coordination columns with fourfold symmetry. Not only is the nature of the anion responsible for distortions in these coordination columns, but it also determines their mutual arrangement. They pack together in such a way as to optimally surround the associated anions with the partially positive amino ends of the thiourea molecules. Spherical (Kruger & Boeyens, 1968) or highly symmetrical (Boeyens & Herbstein, 1967) anions occur in channels among tetragonally arranged coordination columns. Elongated anions such as hydrated fluoride (Boeyens, 1968*a*) require an orthorhombic packing of the columns.

A similar arrangement is encountered in the present structure, the only difference being the oblique cell geometry. In the hydrated complexes, including the chloride complexes (Boeyens, 1968b) the anions can formally be considered as linear rods which line up to form flat sheets parallel to [001] and which can be approached equally closely by amino groups from both sides so as to define an orthogonal channel. In the present circumstances, however, the angular anions cannot line up like this. The resulting sheet contains a 2_1 axis and oxygen atoms which protrude at the edges give a z shaped appearance to the sheet in projection along [001]. To enclose this arrangement of anions by closepacked amine groups an oblique channel and hence monoclinic symmetry are required.

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